U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-298 148

Improvement and Evaluation of Methods for Sulfate Analysis

California State Dept of Health, Berkeley

Prepared for

Environmental Monitoring and Support Lab, Research Triangle Park, NC

Apr 79

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/4-79-028

2.

3. RECIPIENT'S ACCESSION NO.
PB298148

4. TITLE AND SUBTITLE
IMPROVEMENT AND EVALUATION OF METHODS FOR SULFATE ANALYSIS

5. REPORT DATE
April 1979

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
B. R. Appel, E. M. Hoffer, M. Haik, W. Wehrmeister, E. L. Kothny, and J. J. Wesolowski

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Air and Industrial Hygiene Laboratory Section
California Department of Health
2151 Berkeley Way
Berkeley, California 94704

10. PROGRAM ELEMENT NO.
1AD883

11. CONTRACT/GRANT NO.
Grant R-805-447-1

12. SPONSORING AGENCY NAME AND ADDRESS
Office of Research and Development
Environmental Monitoring and Support Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final Report 1977-78

14. SPONSORING AGENCY CODE
EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A simpler and faster procedure for the manual turbidimetric analysis of sulfate has been developed and evaluated. This method as well as a turbidimetric procedure using SulfaVer^{R}, automated methylthymol blue (MTB) procedures for analysis in the 0-100 μg/ml and 0-10 μg sulfate/ml ranges, and the Dionex Ion Chromatograph were evaluated for accuracy, precision, working range, interference effects, and degree of agreement using atmospheric samples. Using EPA sulfate audit strips, all methods showed accuracies within 8% of the accepted value, and coefficients of variation with atmospheric samples of $\leq$ 6%. Colloidal clay and yellow, water soluble organics isolated from atmospheric samples caused interference with all methods. All the methods studied provide reliable analyses for 24-hour hi-vol filter samples. The automated MTB method, modified for use in the 0-10 μg/ml range as suggested by Colovos, offers excellent potential for analysis of low volume samples such as those provided by a dichotomous sampler network.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution and Control Environment Air Monitoring	Measurement Methods Sulfates	68A 43F

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
198

22. PRICE
PC A09 / MF A01

EPA Form 2220-1 (9-73)

United States
Environmental Protection
Agency

Environmental Monitoring and Support
Laboratory
Research Triangle Park NC 27711

EPA-600/4-79-028
April 1979

Research and Development

PB 298148

EPA

Improvement and Evaluation of Methods for Sulfate Analysis

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL MONITORING series. This series describes research conducted to develop new or improved methods and instrumentation for the identification and quantification of environmental pollutants at the lowest conceivably significant concentrations. It also includes studies to determine the ambient concentrations of pollutants in the environment and/or the variance of pollutants as a function of time or meteorological factors.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

EPA-600/4-79-028
April 1979

IMPROVEMENT AND EVALUATION OF METHODS FOR SULFATE ANALYSIS

Final Report

by

B.R. Appel, E.M. Hoffer, M. Haik, W. Wehrmeister,
E.L. Kothny and J.J. Wesolowski
Air and Industrial Hygiene Laboratory Section
California Department of Health Services
2151 Berkeley Way
Berkeley, California 94704

EPA Grant No. R-805-447-1

Project Officer

John C. Puzak
Quality Assurance Branch
Environmental Monitoring and Support Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

A simpler and faster procedure for the manual turbidimetric analysis of sulfate has been developed and evaluated. This method as well as a turbidimetric procedure using SulfaVer^R, automated methylthymol blue (MTB) procedures for analysis in the 0-100 μg/ml and 0-10 μg sulfate/ml ranges, and the Dionex Ion Chromatograph were evaluated for accuracy, precision, working range, interference effects, and degree of agreement using atmospheric samples. Using EPA sulfate audit strips, all methods showed accuracies within 8% of the accepted value, and coefficients of variation with atmospheric samples of $\leq$ 6%. Colloidal clay and yellow, water soluble organics isolated from atmospheric samples caused interference with all methods. All the methods studied provide reliable analyses for 24 hour hi-vol filter samples. The automated MTB method, modified for use in the 0-10 μg/ml range as suggested by Colovos, offers excellent potential for analysis of low volume samples such as those provided by a dichotomous sampler network.

This work is submitted in fulfillment of Grant No. 805-447-1 by the California Department of Health Services under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period October 1, 1977 to September 30, 1978, and work was completed as of September 30, 1978.

CONTENTS

Abstract....................iii

Figures....................v

Tables....................vii

Acknowledgements....................x

I. Introduction....................1

II. Summary and Conclusions....................2

III. Improvement and Evaluation of a $BaSO_4$ Turbidimetric Method 7

IV. Evaluation of an Alternative Turbidimetric Technique Using SulfaVer^R....................59

V. Evaluation of the Midwest Research Institute Version of the Automated Methylthymol Blue Method....................73

VI. Evaluation of the Colovos Modification of the MTB Method..........90

VII. Evaluation of the Dionex Ion Chromatograph....................102

VIII. Effect of Interferents....................115

IX. Intermethod Comparison with Atmospheric Samples....................124

References....................130

Appendices

A. AIHL Method 61-Determination of Sulfate in High Volume Particulate Samples: Turbidimetric Barium Sulfate Method....................131

B. AIHL Method 75 (Draft)-Determination of Sulfate in High Volume Particulate Samples: A Simplified and Improved Barium Sulfate Method....................144

C. Protocol for the Ruggedness Test for Determination of Sulfate by the Turbidimetric Method....................155

D. Protocol for SulfaVer^{R}IV Procedure....................162

E. Tentative Method for the Determination of Sulfates in the Atmosphere (Automated Technicon II Methylthymol Blue Procedure)--prepared by Midwest Research Institute for EPA-EMSL...............163

F. Protocol for Ion Chromatographic Analysis of Sulfate and Nitrate..180

G. Protocol for Extraction of Organics from Aqueous Extracts of Atmospheric Particulates for Use in Interference Studies of Sulfate Methods....................187

FIGURES

Number		Page
1	Comparison of Curve Fitting Procedures with AIHL Method 61 (Trial I)	9
2	Relative Accuracy as a Function of Sulfate Concentration with AIHL Method 61 (Without Sulfate Additions)Third Order Regression for the Working Curve	18
3	Coefficient of Variation as a Function of Sulfate Concentration with AIHL Method 61 (Without Sulfate Additions)Third Order Regression for the Working Curve	19
4	Relative Accuracy as a Function of Sulfate Concentration with AIHL Method 61 (With Sulfate Additions) Third Order Regression for the Working Curve	22
5	Coefficient of Variation as a Function of Sulfate Concentration with AIHL Method 61 (With Sulfate Additions) Third Order Regression for the Working Curve	23
6	Comparison of Curve Fitting Procedures	26
7	Relative Accuracy as a Function of Sulfate Concentration with AIHL Method 75 (Without Sulfate Additions) Third Order Regression for the Working Curve	33
8	Coefficient of Variation of the AIHL Method 75 with Atmospheric Samples (Without Sulfate Additions)	34
9	Relative Accuracy as a Function of Sulfate Concentration with AIHL Method 75 (With Sulfate Additions) Third Order Regression for the Working Curve	37
10	Coefficient of Variation of AIHL Method 75 With Atmospheric Samples (With Sulfate Additions)	38
11	Comparison of Working Curves with Varying $BaCl_2$ Samples Using AIHL Method 75	47
12	The Effect of $BaCl_2 \cdot 2H_2O$ Particle Size on the Slope for the Working Curve AIHL Method 75	52
13	Micrographs of Three Samples of 40-50 Mesh Barium Chloride	57
14	Reproducibility of Working Curve for SulfaVer^R Method	66
15	Relative Accuracy as a Function of Sulfate Concentration with SulfaVer^R (Third Order Regression for the Working Curve)	71
16	Coefficient of Variation as a Function of Sulfate Concentration (Third Order Regression for the Working Curve) SulfaVer^R Method	72
17	MTB Assay by Midwest Research Institute Procedure-February 2, 1978	75

18 Working Curve for MRI-MTB Procedure-February 27, 1978 79

19 Relative Accuracy as a Function of Concentration for the MRI-MTB Method 88

20 Coefficient of Variation as a Function of Concentration for the MRI-MTB Method 89

21 Comparison of Working Curves as a Function of Ba/MTB Ratio 94

22 Typical Working Curve for Colovos-MTB Method in 0-10 μg/ml Range 96

23 Relative Accuracy as a Function of Sulfate Concentration with the Colovos-MTB Method 100

24 Coefficient of Variation as a Function of Sulfate Concentration with the Colovos-MTB Method 101

25 Resolution of Sulfate and Nitrate at Equal Concentrations by Ion Chromatography 103

26 Reproducibility of Working Curve for Dionex Ion Chromatograph (Range: 10 μmho) 106

27 Comparison of Working Curves for Dionex Ion Chromatograph on Ranges 1, 3 and 10 μmho 107

28 Regression Equation Slope Against μmho for Full Scale with Dionex Ion Chromatograph 109

29 Relative Accuracy as a Function of Sulfate Concentration with the Dionex Ion Chromatograph (Range 10 μmho) 113

30 Coefficient of Variation as a Function of Sulfate Concentration with the Dionex Ion Chromatograph (Range 10 μmho) 114

31 Scatter Diagrams of Results With Atmospheric Sample Using Five Sulfate Methods 129

TABLES

Number		Page
1	Summary of Methods Evaluations	5
2	Curve Fitting as a Function of Concentration for AIHL Method 61 $BaSO_4$ Turbidimetric Method Without Sulfate Additions Using Log-Log and Linear Regression	11
3	Curve Fitting as a Function of Concentration for AIHL Method 61 $BaSO_4$ Turbidimetric Method Without Sulfate Additions Using Third Order Regression	12
4	Accuracy as a Function of Concentration for AIHL Method 61 $BaSO_4$ Turbidimetric Method with 300 μg/20 ml Sulfate Addition and Linear Regression	14
5	Accuracy as a Function of Concentration for AIHL Method 61 $BaSO_4$ Turbidimetric Method with 300 μg/20 ml Sulfate Addition and Third Order Regression	15
6	Relative Accuracy and Precision of AIHL Method 61 $BaSO_4$ Turbidimetric Method (without Sulfate Additions) with an Atmospheric Sample (μg $SO_4^=$/20 ml solution)	17
7	Relative Accuracy and Precision of AIHL Method 61 $BaSO_4$ Turbidimetric Method (with Sulfate Additions) with an Atmospheric Sample (μg $SO_4^=$/20 ml Solution)	21
8	Curve Fitting as a Function of Concentration AIHL Method 75 Without Sulfate Additions Log-Log and Linear Regression	27
9	Curve Fitting as a Function of Concentration AIHL Method 75 Without Sulfate Additions Third Order Regression	28
10	Accuracy as a Function of Concentration for the AIHL Method 75 with 300 μg/20 ml Sulfate Addition and Linear Regression	29
11	Relative Accuracy and Precision of the AIHL Method 75 (without Sulfate Additions) with Atmospheric Samples (μg $SO_4^=$/20 ml solution)	32
12	Relative Accuracy and Precision of AIHL Method 75 (with Sulfate Additions) with Atmospheric Samples (μg $SO_4^=$/20 ml solution)	36
13	Analysis of EPA Sulfate Audit Strips by the AIHL Method 75	39
14	Summary of Results of Turbidimetric Methods	41
15	Factors for Evaluation in Ruggedness Test	43
16	Results of Ruggedness Test of Sulfate Analysis by Turbidimetry	44
17	Description of $BaCl_2$ Used for Turbidimetric Method	48

18 Size Distribution of J. T. Baker $BaCl_2 \cdot 2H_2O$ (% by Weight) 49

19 Working Curves for Method 75 Turbidimetric Method With Size Fractionated $BaCl_2 \cdot 2H_2O$ (Linear Regression) 51

20 Comparison of Observed Working Curve Slopes for AIHL Method 75 With Those Calculated from Individual Fractions 53

21 Analysis of $BaCl_2 \cdot 2H_2O$ for Trace Metals (ppm by Weight) 55

22 Comparison of Dissolving Times for Three Samples of $BaCl_2$ 56

23 Conditions Studied in Developing Protocol for SulfaVer^R IV Procedure 60

24 Influence of Protocol Variables on the Working Curve Using SulfaVer^R IV (Third Order Regression) 62

25 Influence of Protocol Variables on the Working Curve Using SulfaVer^R IV (Linear Regression) 63

26 Curve Fitting as a Function of Concentration Using a SulfaVer^R IV Procedure 65

27 Reproducibility of Working Curve for SulfaVer^R Method (Third Order Regression) 67

28 Analysis of EPA Sulfate Audit Strips by a SulfaVer^R Method 68

29 Relative Accuracy and Precision of SulfaVer^R Turbidimetric Method With an Atmospheric Sample (μg SO_4^{2-}/20 ml) 70

30 Calculation of MTB Purity 77

31 Assay of MTB by Midwest Research Institute Method 78

32 Reproducibility of Calibration: Sulfate by MRI-MTB Method 80

33 Curve Fitting as a Function of Concentration for the MRI-MTB Method 82

34 Effect of a 5% Error in MTB Assay Upon the Calibration Curve for the MRI-MTB Method 83

35 Analysis of EPA Sulfate Audit Strips by the MRI-MTB Method 84

36 Relative Accuracy and Precision of MRI-MTB Method With an Atmospheric Sample (μg $SO_4^=$/ml)Linear Regression 86

37 Relative Accuracy and Precision of MRI-MTB Method With an Atmospheric Sample (μg $SO_4^=$/ml) Third Order Regression 87

38 Straight Line Fitting as a Function of Concentration for the Colovos-MTB Method (% Error) 92

39 Reproducibility and Linearity of the Working Curve for the Colovos-MTB Method (0-10 μg/ml) 95

40 Analysis of Sulfate EPA Audit Strips by the Colovos-MTB Method 98

41 Relative Accuracy and Precision of Colovos-MTB Method With an Atmospheric Sample (μg $SO_4^=$/ml) 99

42 Reproducibility of Working Curve for Dionex Ion Chromatograph (Range: 10 μmho) 105

43 Analysis of EPA Sulfate Audit Strips by the Dionex Ion Chromatograph 110

44 Relative Accuracy and Precision of the Dionex Ion Chromatograph, Range 10 μmho (μg $SO_4^=$/ml) 112

45 Sulfate and Interferent Levels for Interference Studies 116

46 Interference Effect With the AIHL Method 75 (μg/ml Observed Sulfate) 118

47 Interference Effects With the MRI-MTB Method 119

48 Interference Effect With the Colovos MTB Method (μg/ml Observed Sulfate) 121

49 Interference of Nitrate in Sulfate Determination With the Dionex Ion Chromatograph 123

50 Description of 24 Hour Hi-Vol Filter Samples for Intermethod Comparison 125

51 Results of Intermethod Comparison With Atmospheric Samples (μg/ml) 127

52 Average Agreement and Precision of Methods With Atmospheric Samples 128

ACKNOWLEDGEMENTS

Other participants in this study included Ms. S. Twiss who supervised data reduction and Ms. L. Raftery who provided capable assistance in the laboratory.

The atmospheric samples used in this study were provided by Mr. J. Wendt, California Air Resources Board. His cooperation and assistance are gratefully acknowledged.

Mr. J. C. Puzak served as Project Officer for this program. His helpfulness throughout this work has been sincerely appreciated.

I. INTRODUCTION

In preceding EPA-sponsored programs, a series of wet chemical sulfate methods was evaluated and compared to total sulfur determinations by x-ray fluorescence analysis.[1,2] These methods were:

--A barium sulfate turbidimetric procedure (Public Health Service Version)[3]

--An automated methylthymol blue (MTB) procedure[4]

--The AIHL microchemical method[5,6]

--Two modifications of the thorin method as developed by C. Brosset[7]

--A manual barium chloranilate method[8].

The current program continued these studies employing improved or alternative versions of some of these procedures. The specific objectives included, (1) improving and evaluating for ruggedness a barium sulfate turbidimetric method (AIHL Method 61) for sulfate analysis, and (2) an evaluation of a series of sulfate methods for comparability, accuracy, precision, working range and effect of interferences. These methods were: a barium sulfate turbidimetric method using SulfaVer[R], the Midwest Research Institute version of the MTB method[10], the MTB method as modified by Colovos for analysis in the 0-10 μg/ml range[11], and the Dionex ion chromatograph.[12]

II. SUMMARY AND CONCLUSIONS

Modification of the AIHL Method 61, a version of the $BaSO_4$ turbidimetric method, to permit reaction of samples in inexpensive, capped test tubes directly usable for measurement of turbidity eliminates the need for multiple transfers of samples. The resulting procedure, designated AIHL Method 75, showed slightly improved precision and increased accuracy in the non-linear range below 300 μg sulfate/20 ml solution when using third order regression techniques. The addition of fixed quantities of sulfate to low concentration samples (to permit their analysis in the nearly linear region of the working range) was found inferior to direct analysis using third order fitting of the working curve. Defining the working range as that providing approximately constant relative accuracy* and coefficient of variation, for Method 75 the working range was from 140 to at least 1400 μg $SO_4^=$/20 ml samples (7 to 70 μg $SO_4^=$/ml) using third order regression.

An eleven parameter ruggedness test was performed utilizing the procedures of both AIHL Methods 61 and 75 to reveal areas contributing to variability in sulfate determinations by turbidimetric methods. From this test only the age of the pre-mixed glycerin-HCl-water reagent was found to be a statistically significant contributor to such variability.

Methods 61,75, and similar procedures call for use of crystalline barium chloride dihydrate specified by its manufacturer as being "For Parr turbidimeter" with or without a specified mesh size (e.g. 20 mesh in the Old U.S. Series mesh size). The current unavailability of barium chloride graded for use in turbidimetric sulfate analyses prompted an investigation of the influence of mesh size and impurities in $BaCl_2 \cdot 2H_2O$ on its suitability for these analyses. The ideal barium chloride was considered to be one yielding linear working curves with relatively high slope values, small intercepts and little scatter. It was determined that size-fractionated $BaCl_2$ is not mandatory for turbidimetric analyses. For a given reagent, the resulting working curve slope increased with increasing $BaCl_2 \cdot 2H_2O$ particle size. Differences in results between reagents with the same mesh size were explained by differences in the crystals in the aggregates composing the particles, e.g. smaller crystal size promoted more rapid dissolution rates with correspondingly increased slopes.

---

*The analytical results of the method with an atmospheric sample of varying dilution relative to that obtained for the same sample in the optimal concentration range of the method.

A study of an alternative turbidimetric procedure utilizing SulfaVer^R, a mixture of barium chloride crystals and a proprietary colloid stabilizing agent, was included in this program. After optimizing the analytical protocol, an evaluation of this procedure yielded similar results to those for Method 75.

Studies of the automated methylthymol blue (MTB) procedures included evaluations of the Midwest Research Institute (MRI) method for 0-100 μg/ml sulfate and the modification made by G. Colovos and co-workers for 0-10 μg/ml sulfate. The working range for the MRI-MTB procedure, while expanded at the upper end, was notably compressed at the lower end relative to the version of the MTB procedure previously evaluated.[2] The latter permitted analysis down to 7 μg/ml (linear regression) and to ca. 4 μg/ml with third order regression. Modification of the MRI procedure to eliminate a sample memory effect as a cause of its reduced range is here recommended.

Both the MRI and Colovos methods employ relatively time consuming procedures for achieving more nearly linear working curves. The MRI procedure yielded a working curve which was fit substantially better by two straight lines or third order regression than by a single line. The Colovos procedure yielded working curves in the 0-10 μg/ml with acceptable linearity (e.g. correlation coefficient = 0.997 for a least squares line).

The Dionex IC chromatograph, thermostated for use at 35°C, provided sulfate determination with generally lower accuracy and precision compared to the other methods. Peak heights provided somewhat better precision and accuracy compared to integrated peak areas. A small positive interference from nitrate was identified as one source of decreased accuracy.

Colloidal clay, water soluble yellow organics isolated from atmospheric particulate matter, phosphate and bicarbonate were evaluated as potential interferents with turbidimetric and methylthymol blue methods. Colloidal clay and organics caused interference in all cases studied but with differing sign.

Table 1 summarizes results for the methods studied with respect to accuracy and precision, the concentration ranges providing relative accuracy and precision within 10% and 5%, respectively, and the effect of interferences.

Table 1

Summary of Methods Evaluations

Method	EPA Audit Strips Mean Obs/Theoret.	 Mean C.V. (%)[a]	Concentration Range for Relative Accuracy Within 10% and C.V. < 5% (µg/ml)	Significant Interferent Positive	 Negative
Method 75	1.04	3.8	10 to $\geq$ 70[b]	---	colloidal clay, organics
SulfaVer^{R}	1.06	3.6	9 to $\geq$ 70[b]	not determined	
MRI-MTB (linear regression)	1.06	2.8	17 to $\geq$ 90	not determined	
MRI-MTB (third order)	1.04	3.4	14 to $\geq$ 90	colloidal clay, organics	---
Colovos-MTB	0.98	1.3	2 to $\geq$ 10	colloidal clay, organics	---
Dionex-IC (Range 10 µmho)	1.08	6.2	7 to 130[c]	nitrate	---

---

a. Coefficients of variation for samples within working range of method.

b. Employing 20 ml samples.

c. Working range as defined by concentration range providing approximately constant relative accuracy and C.V. was 7 to 111 µg/ml.

An intermethod comparison with the methods cited in Table 1 plus the AIHL microchemical sulfate method[7,9] using 24 hi-vol filter sample extracts demonstrated, on average, agreement within 10% for all methods.

The regression equations relating results between the Method 75 and the other procedures are as follows:

SulfaVer = 1.10 (Method 75) - 0.570 $r = 0.998$ $S_{y.x} = 3.00$

MRI-MTB = 1.06 (Method 75) - 0.759 $r = 0.997$ $S_{y.x} = 3.43$

Colovos MTB = 1.01 (Method 75) + 0.774 $r = 0.999$ $S_{y.x} = 1.72$

Dionex IC = 1.08 (Method 75) - 0.022 $r = 0.998$ $S_{y.x} = 2.76$

AIHL Micro = 1.06 (Method 75) + 0.851 $r = 0.998$ $S_{y.x} = 2.54$

The present study indicates that Method 61, Method 75, SulfaVer^{R}, Dionex IC (range 10 μmho) and the automated MRI-MTB methods are suitable for analysis of hi-vol samples. Choice between methods should reflect equipment availability and number of samples. The MRI-MTB procedure can probably be improved by decreasing the samples per hour. For low volume samples the present study suggests that the Colovos-MTB method is suitable if at least 4 ml of solution in the range 2 to 10 μg/ml is available.*
As such, it may be the wet chemical method of choice for sulfate analysis of samples from a dichotomous sampler network.

---

*For comparison, the manual AIHL microchemical method requires $\leq$ 1 ml of sample in the range from about 1 to 15 μg/ml.

III. IMPROVEMENT AND EVALUATION OF $BaSO_4$ TURBIDIMETRIC METHOD

A. Introduction

Efforts to improve the turbidimetric method were focused on three aspects:

- --The addition of a known amount of barium sulfate to all samples to eliminate reliance on the non-linear portion of the working curve.

- --Mixing of reagents and samples in inexpensive, screw-capped test tubes suitable for measuring turbidity, eliminating the need for multiple transfers from graduated cylinders prior to determining turbidity values.

- --Use of a relatively inexpensive spectrophotometer (B&L 20) in place of a B&L 70.

The specific parameters included in the evaluation methods were, 1) reproducibility and linearity of the working curve, 2) accuracy and precision using EPA audit samples (glass fiber filter strips spiked with known quantities of sulfate), 3) working concentration range, and 4) addition of fixed quantities of sulfate to samples to permit analyses of low sulfate concentration samples in the linear region of the working curve (see below).

The standard of comparison for the current efforts to provide an improved turbidimetric procedure was the Air and Industrial Hygiene Laboratory Method 61 (Revised July 1976). The procedure is included as Appendix A.

B. Evaluation of AIHL Method 61

1. Evaluation of Working Curves Without Sulfate Addition

In AIHL Method 61 the reaction of sulfate with barium is carried out in graduated cylinders with transfers to a 20 mm diameter cuvet for measurements using a B&L Spectronic 70.

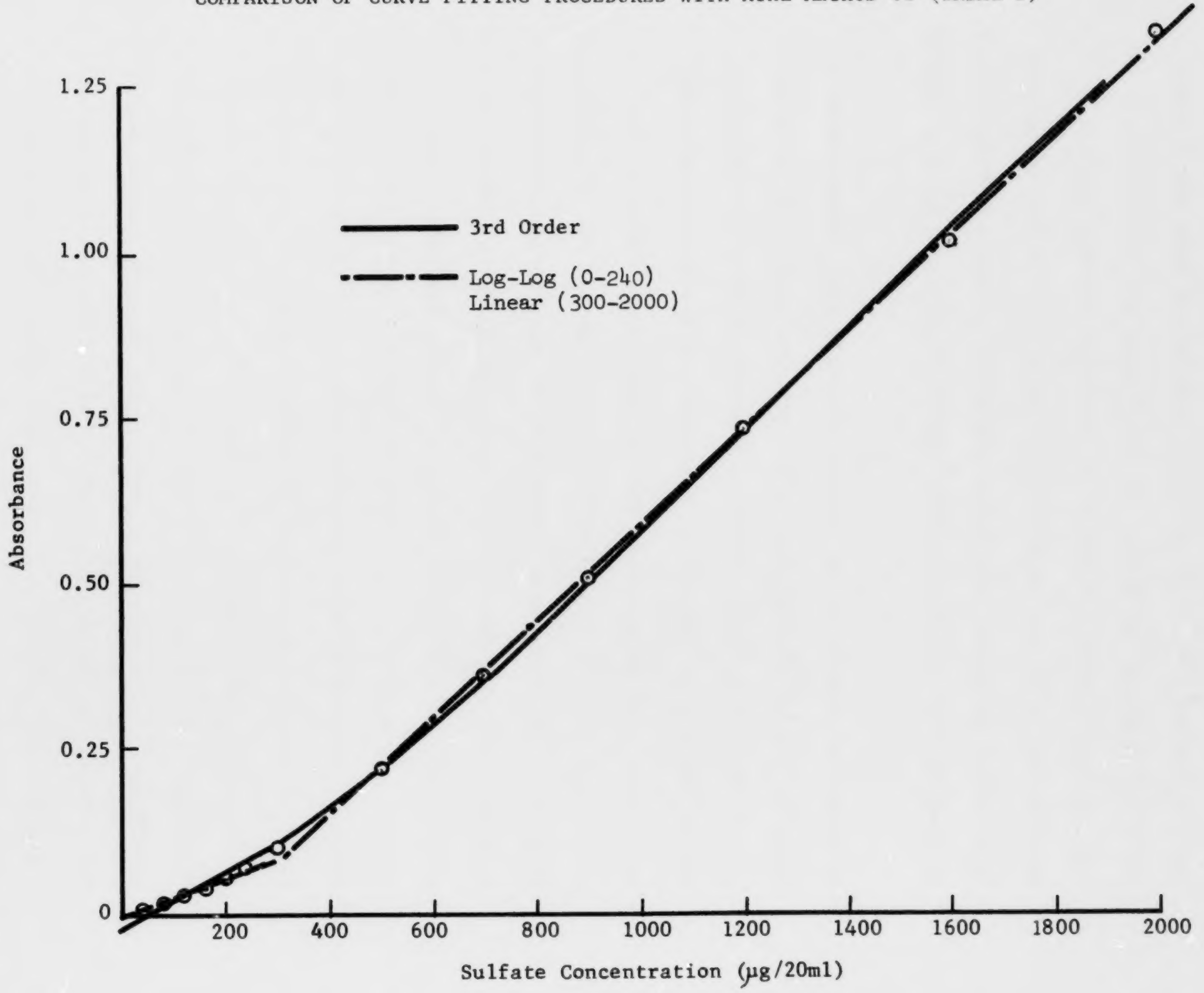
Working curves were prepared, in three trials covering the concentration range 40-2000 μg sulfate/20 ml. Standards and samples were dispensed in 10 ml of water followed by 10 ml of distilled water.* This contrasts with the usual procedure which employs 20 ml of samples or standards. In the present study, observed concentrations expressed as μg/20 ml are equal to the μg/10 ml of the initial sample. As written, Method 61 employs linear regression in the range 300-1000 μg/20 ml and restricts the working curve to levels $\leq$ 1500 μg/20 ml because of reported non-linearity. No evidence of non-linearity was observed in the present study up to 2000 μg/20 ml. Below 300, the curve is non-linear and a graphical method of data reduction is recommended. The present evaluation employed non-linear regression techniques to provide more objective results for method comparison. Two curve fitting procedures were evaluated: 1) A log-log fit for the range 40-240 μg/20 ml followed by linear regression in the range 300-2000 μg/20 ml, and 2) a single third order polynomial fit throughout the range. Figure 1 illustrates the results for one trial. The regression equations and the average goodness of fit by the two procedures as a function of concentration are given

---

*For trials with sulfate addition, the 10 ml of distilled water was replaced by 10 ml of solution containing a known amount of sulfate.

Figure 1

COMPARISON OF CURVE FITTING PROCEDURES WITH AIHL METHOD 61 (TRIAL I)



in Tables 2 and 3. These results show that:

1) third order regression curve fitting is adequate down to 80 μg/20 ml and the log-log fit, to 40 μg/ml, 2) considering both mean % error and coefficient of variation, the third order fit is superior to the log-log fit + linear regression for the range 80-2000 μg/20 ml sulfate, and 3) in the range 300-2000 μg/20 ml, the % error by both third order and linear regression averaged + .2 and -.2, respectively. In general, the two curve fitting procedures differed by less than 3%.

Although the results by the log-log fit imply that analysis down to 40 μg/20 ml might be feasible, additional perspective on the lower end of the working range with standards was obtained by considering the variability in the initial turbidity reading (read as % transmission, T_1, and subsequently recalculated as absorbance). Our experience with the turbidimetric method suggests that an uncertainty of up to ± .5% transmittance exists due to such variables as residual bubbles, colloidal matter in the sample and slight variations in positioning the cell in the holder of the spectrometer. This sharply increases the coefficient of variation at low levels. For example, assuming no imprecision in value for T_2 (after $BaCl_2$ addition), the results indicate at 160 μg/20 ml a C.V. of 40% due only to this estimated maximum uncertainty in T_1, the value increasing to 80% at 40 μg/20 ml. This source of imprecision may be especially significant when the method is not carried out with maximum care. The present work is being carried out with the greatest possible effort to minimize such sources of imprecision. The above calculation, therefore, is not considered relevant to the current

Table 2

Curve Fitting as a Function of Concentration for AIHL Method 61 $BaSO_4$ Turbidimetric Method Without Sulfate Additions Using Log-Log and Linear Regression

True Sulfate µg/20 ml	Mean Observed $SO_4^{=a}$	C.V.(%)	$\frac{\text{Mean Obs. } SO_4^=}{\text{True } SO_4^=}$	Mean % Error[b]
40	45.1 ± 5.5	12.2	1.13	12.8
80	69.3 ± 6.8	9.8	0.87	- 13.4
120	113.8 ± 9.5	8.3	0.95	- 5.2
160	156.3 ± 3.3	2.1	0.98	- 2.3
200	201.2 ± 11.1	5.5	1.01	0.6
240	266.9 ± 21.4	8.0	1.11	11.2
300	318.9 ± 13.4	4.2	1.06	6.3
500	482.0 ± 8.2	1.7	0.96	- 3.6
700	672.7 ± 12.8	1.9	0.96	- 3.9
900	890.1 ± 32.0	3.6	0.99	- 1.1
1200	1255 ±105	8.4	1.05	4.6
1600	1594 ± 11.1	0.7	1.00	- 0.4
2000	1988 ± 37.8	1.9	0.99	- 0.6

Coefficients for Regression Equations

For $SO_4^= < 300$ µg/20 ml $(SO_4^=) = a\,(\text{Absorbance})^b$					For $SO_4^= \geq 300$ µg/20 ml $(SO_4^=) = c + d\,(\text{Absorbance})$			
Trial	a	b	r	$S_{y.x}$	c	d	r	$S_{y \cdot x}$
I	.000077	1.23	.998	.028	-.137	.000722	.9996	0.0136
II	.000051	1.29	.995	.040	-.123	.000712	.9995	0.0145
III	.000157	1.08	.957	.106	-.127	.000744	.9920	0.0635

---

a. Calculated from the regression equations, µg/20 ml.

b. [(mean obs. - true)/(true sulfate)] x 100

Table 3

Curve Fitting as a Function of Concentration for AIHL Method 61 $BaSO_4$ Turbidimetric Method Without Sulfate Additions Using Third Order Regression

True Sulfate µg/20 ml	Mean Observed $SO_4^=$	C.V.(%)	$\frac{\text{Mean Obs. } SO_4^=}{\text{True } SO_4^=}$	Mean % Error
40	75.4 ± 4.7	6.2	1.89	88.5
80	90.6 ± 8.5	9.4	1.13	13.2
120	121.6 ± 4.9	4.0	1.01	1.3
160	151.5 ± 2.1	1.4	0.95	- 5.3
200	182.4 ± 10.6	5.8	0.91	- 8.8
240	226.3 ± 11.3	5.0	0.94	- 5.7
300	291.6 ± 7.9	2.7	0.97	- 2.8
500	495.5 ± 6.9	1.4	0.99	- 0.9
700	697.2 ± 11.9	1.7	1.00	- 0.4
900	906.3 ± 39.9	4.4	1.01	- 0.7
1200	1235 ± 60.5	4.9	1.03	2.9
1600	1555 ± 37.3	2.4	0.97	- 2.8
2000	2038 ± 46.9	2.3	1.02	1.9

Coefficients for Regression Equation

$$SO_4^= = e + fx + gx^2 + hx^3 \qquad \text{For } 40 \le SO_4^= \le 2000\ \mu g/ml$$

Trial	e	f	g	h	r	$S_{y \cdot x}$
I	-1.89×10^{-2}	3.33×10^{-4}	3.42×10^{-7}	-0.874×10^{-10}	.99997	.0119
II	-2.19×10^{-2}	3.35×10^{-4}	3.69×10^{-7}	-1.04×10^{-10}	.99996	.0138
III	-4.87×10^{-3}	1.66×10^{-4}	6.97×10^{-7}	-2.26×10^{-10}	.9997	.0378

program, but may offer insight relevant to ruggedness testing.

2. The Accuracy of AIHL Method 61 with Sulfate Addition

In place of 10 ml of distilled water three hundred µg of sulfate in 10 ml water was added to each of a set of pure sulfate solutions covering the range 40 to 1600 µg/20 ml. The resulting solutions were analyzed by AIHL Method 61 using both linear and third order regression for working curves in the range 300-2000 µg/20 ml. The mean results for three trials, after subtracting the sulfate added, are compared to the true sulfate values in Tables 4 and 5.

The accuracy with standards, adding fixed quantities of sulfate, was generally excellent. The accuracy using third order regression for standards ranging from 40 to 500 µg/20 ml was significantly better than with linear regression but the precision was generally poorer in this range as well as above 500 µg/20 ml.

These results may be compared to the goodness of fit to the non-linear working curves below 300 µg/20 ml, given in Table 3, as a measure of the accuracy of the method without addition of fixed amounts of sulfate.

In the range 80-240 µg/20 ml the mean error (using absolute values for the values given in the Table) with addition of fixed quantities of sulfate is 1.2% and 3.9% by third order and linear regression, respectively. This compares to a mean error of 5.1% for the log-log and third order fit of the working curve (without addition of sulfate) in the range 80-240 µg/20 ml.

Table 4

Accuracy as a Function of Concentration for AIHL Method 61 $BaSO_4$ Turbidimetric Method with 300 μg/20 ml Sulfate Addition and Linear Regression[a]

True Sulfate less 300 (μg/20 ml)	Mean Observed $SO_4^=$ [b] (μg/20 ml)	C.V.	Mean Obs. $SO_4^=$ / True Sulfate ± σ[c]	Mean % Error[d]
40	47.0 ± 6.9	14.6	1.174 ± .172	+ 17.5
80	80.7 ± 6.1	7.5	1.009 ± .077	+ 0.9
120	118.0 ± 6.2	5.3	0.983 ± .053	- 1.7
160	153.4 ± 15.6	10.2	0.958 ± .098	- 4.1
200	186.0 ± 10.5	5.7	0.930 ± .053	- 7.0
240	225.6 ± 14.0	6.2	0.940 ± .059	- 6.0
300	291.7 ± 14.1	4.8	0.972 ± .048	- 2.8
500	482.1 ± 16.1	3.3	0.964 ± .034	- 3.6
700	693.6 ± 10.2	1.5	0.991 ± .018	- 0.9
900	900.3 ± 21.2	2.4	1.000 ± .026	0.0
1200	1218 ± 9.2	0.8	1.015 ± .013	+ 1.5
1600	1597 ± 20.1	1.3	0.998 ± .016	- 0.2

Coefficients for the Linear Working Curve

Trial	a	b	r	$S_{y.x}$
I	-.123	0.000737	0.9925	0.0608
II	-.134	0.000729	0.9996	0.0131
III	-.138	0.000731	0.9997	0.0124

a. A linear regression curve was prepared from 6 points in the range 300-2000 μg/20 ml. An independent set of samples was prepared from sulfate standard solutions covering the range shown. To each sample, 300 μg sulfate was added, the total sulfate determined from the working curve and 300 μg subtracted from the resulting values.

b. Obtained for three independent trials.

c. A precision of ± 1% was estimated for the "true sulfate" concentration to calculate σ values.

d. $\frac{\text{Mean Obs.-True}}{\text{True}} \times 100$

Table 5

Accuracy as a Function of Concentration for AIHL Method 61 $BaSO_4$ Turbidimetric Method with 300 µg/20 ml Sulfate Addition and Third Order Regression[a]

True Sulfate less 300 (µg/20 ml)	Mean Observed $SO_4^=$[b] (µg/20 ml)	C.V.	$\frac{\text{Mean Obs. } SO_4^=}{\text{True Sulfate}}$ ± σ[c]	Mean % Error[d]
40	41.4 ± 13.1	31.7	1.036 ± .328	+ 1.0
80	80.5 ± 11.2	13.9	1.006 ± .140	+ 0.6
120	122.5 ± 11.3	9.2	1.020 ± .095	+ 2.1
160	162.0 ± 4.8	3.0	1.012 ± .032	+ 1.3
200	196.9 ± 2.6	1.3	0.985 ± .016	- 1.6
240	239.0 ± 7.9	3.3	0.996 ± .034	- .4
300	307.3 ± 11.7	3.8	1.024 ± .040	+ 2.4
500	495.1 ± 23.7	4.8	0.990 ± .048	- 1.0
700	694.5 ± 27.0	3.9	0.992 ± .040	- 0.8
900	886.5 ± 43.0	4.9	0.985 ± .049	- 1.5
1200	1187.9 ± 32.2	2.7	0.990 ± .029	- 1.0
1600	1597.3 ± 7.6	0.5	0.998 ± .011	0.2

Coefficients for Third Order Working Curve

Trial	a	b	c	d	r	$S_{y.x}$
I	-8.104×10^{-2}	4.635×10^{-4}	3.820×10^{-7}	-1.333×10^{-10}	0.9982	.0675
II	-4.865×10^{-2}	4.253×10^{-4}	2.893×10^{-7}	-0.796×10^{-10}	0.9999	.00250
III	-5.830×10^{-2}	4.428×10^{-4}	2.803×10^{-7}	-0.784×10^{-10}	0.9999	.00228

a. A third order regression curve was prepared from 6 points in the range 300-2000 µg/20 ml. An independent set of samples was prepared from sulfate standard solutions covering the range shown. To each sample, 300 µg sulfate was added, the total sulfate determined from the working curve and 300 µg subtracted from the resulting values.

b. Obtained for three independent trials.

c. A precision of ± 1% was estimated for the "true sulfate" concentration to calculate σ values.

d. $\frac{\text{Mean Obs.-True}}{\text{True}} \times 100$

3. Working Range Without Sulfate Additions

A single atmospheric sample extract was prepared by pooling a large number of single filter extracts. The resulting solution was centrifuged cold at 6000 rpm to remove suspended particles and diluted to varying degrees to permit evaluation of the "relative accuracy" and precision as a function of concentration. The term relative accuracy reflects the accuracy of the analysis at a given degree of dilution relative to the analytical results from analyses done in what is considered the optimal concentration range of the method. Relative accuracy and precision were used to evaluate the working range of the sulfate method (i.e., the concentrations which show both approximately constant relative accuracy and coefficient of variation).

The results of the Method 61, without addition of standard amounts of sulfate, are compiled in Table 6, employing third order regression of the working curve. The calculated, undiluted concentration of the extract showed no apparent bias between 15 and 100% concentration. Thus, the correct undiluted concentration was taken to be the mean of seven results, 1418 ± 49 μg/20 ml. The ratio of observed to expected concentrations are plotted against expected concentration in Figure 2. The results indicate accuracy within 7% of the optimal value in the concentration range from 71 to 1418 μg/20 ml. The coefficient of variation of three independent trials is plotted against expected concentration in Figure 3. The C.V. values remain less than 8% in the range 106 to 1418 μg/20 ml.

Table 6

Relative Accuracy and Precision of AIHL Method 61 $BaSO_4$ Turbidimetric Method (without Sulfate Additions) with an Atmospheric Sample ($\mu g\ SO_4^{=}/20$ ml solution)

Concentration, % of Undiluted	Observed Mean of 3 Trials	σ	σ^2	C.V. (%)[a]	Calculated Undiluted Concentration	Expected Diluted Concentration[b]	Observed Conc. / Expected Conc.
2.5	67.7	4.8	22.6	7.0	2709.5	35.5	1.910
5.0	75.8	13.7	187.0	18.1	1515.2	70.9	1.068
7.5	108.1	2.5	6.4	2.3	1441.8	106.4	1.017
10.0	139.4	9.2	83.7	6.6	1394.4	141.8	0.983
12.5	160.1	12.5	155.1	7.8	1280.8	177.3	0.903
15.0	206.9	11.6	134.6	5.6	1379.3	212.7	0.973
18.75	250.5	8.1	66.4	3.2	1335.9	265.9	0.942
31.25	436.1	11.7	137.7	2.7	1395.5	443.2	0.984
43.75	631.0	2.9	8.7	0.5	1442.3	620.5	1.017
56.25	827.1	8.1	64.9	1.0	1470.3	797.7	1.037
75.0	1091.9	18.8	352.8	1.7	1455.9	1063.7	1.027
100	1448.3	8.4	70.2	0.6	1448.2	1418.2	1.021

Mean undiluted conc. = 1418 ± 49

Coefficients for Third Order Working Curves

Trial	a	b	c	d	$S_{y.x}$
I	-2.042×10^{-2}	3.365×10^{-4}	3.566×10^{-7}	-9.502×10^{-11}	0.0065
II	-2.098×10^{-2}	3.443×10^{-4}	3.429×10^{-7}	-9.320×10^{-11}	0.0100
III	-1.351×10^{-2}	2.963×10^{-4}	4.165×10^{-7}	-11.53×10^{-11}	0.0050

a. (σ/mean) x 100

b. Equals (Mean undiluted conc.) x (Concentration, % of undiluted) x .01.

Figure 2

RELATIVE ACCURACY AS A FUNCTION OF SULFATE CONCENTRATION
WITH AIHL METHOD 61 (WITHOUT SULFATE ADDITIONS)
THIRD ORDER REGRESSION FOR THE WORKING CURVE

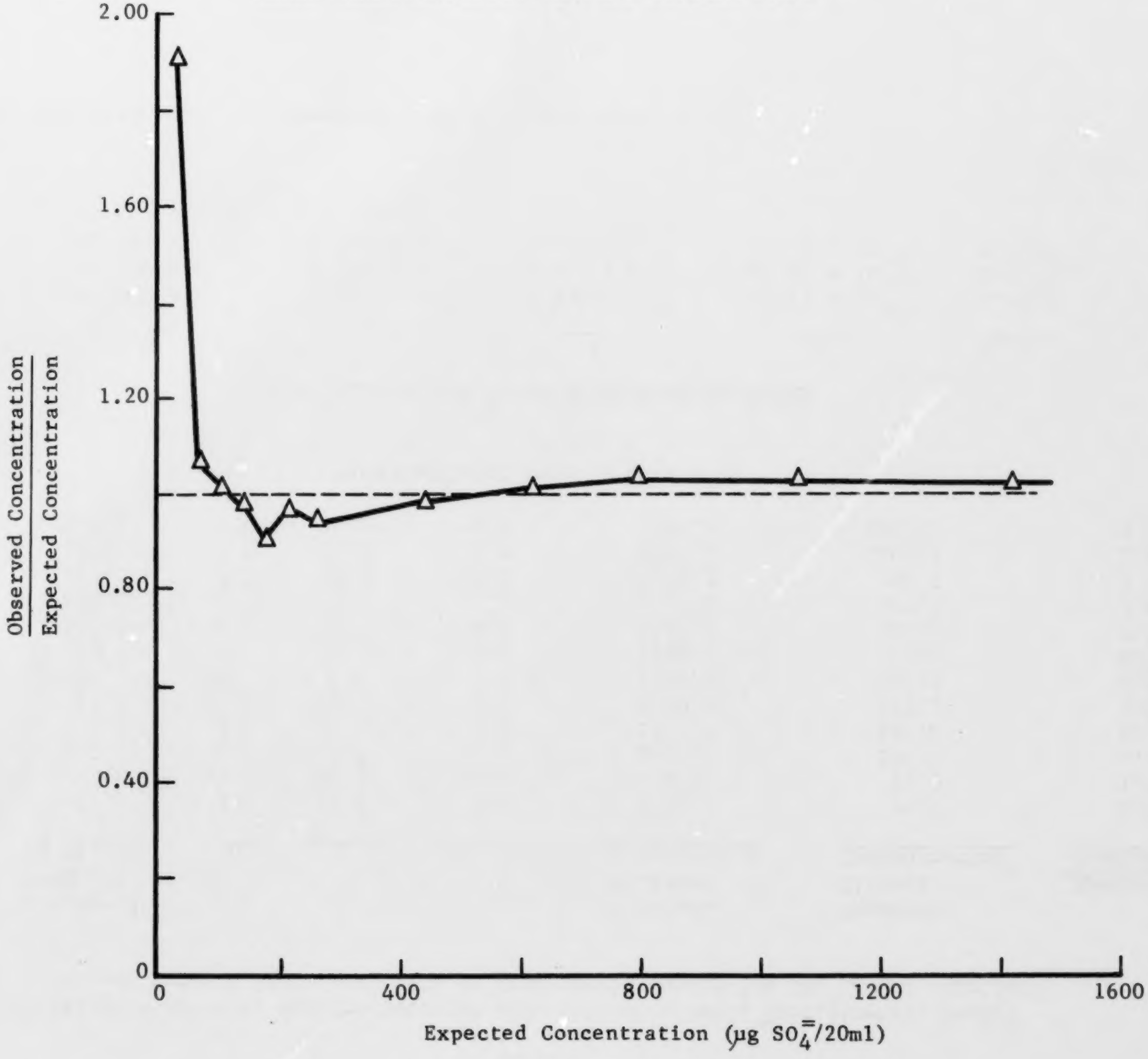
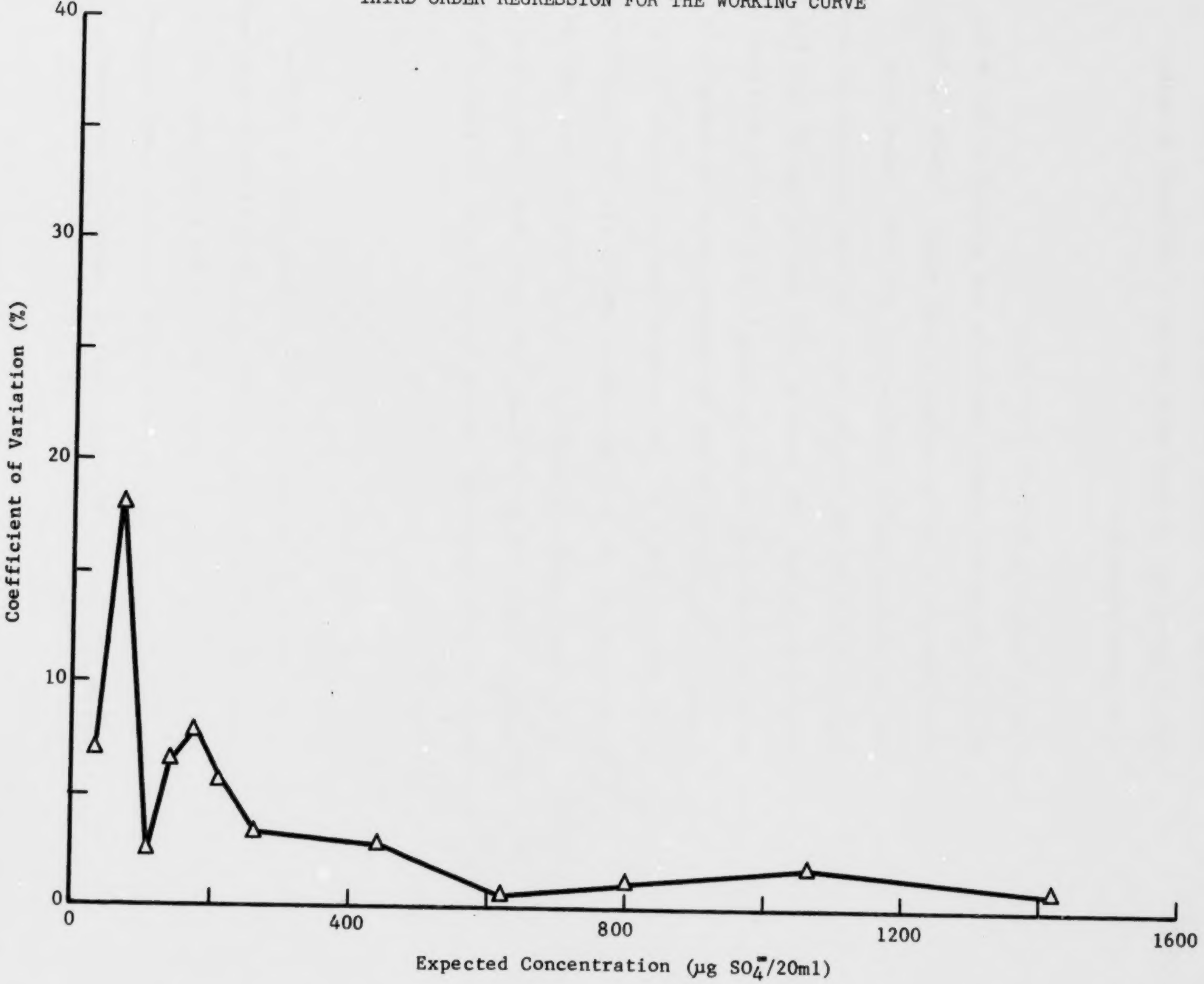


Figure 3

COEFFICIENT OF VARIATION AS A FUNCTION OF SULFATE CONCENTRATION
WITH AIHL METHOD 61 (WITHOUT SULFATE ADDITIONS)
THIRD ORDER REGRESSION FOR THE WORKING CURVE



Based on both relative accuracy and precision as measured by coefficient of variation, the working range of Method 61, without sulfate additions, is from about 100 to $\geq$ 1400 μg/20 ml using third order regression.

4. Working Range with Sulfate Addition

The same atmospheric sample used above was analyzed by the Method 61 after addition of 300 μg sulfate to each sample. Since the data analysis without sulfate addition was done with a third order regression fit for the working curve, the same procedure was used with added sulfate. The results, after subtracting 300 from the observed sulfate, are shown in Table 7. The correct, undiluted sulfate concentration for the atmospheric sample was taken to be 1418 μg/20 ml (Table 6). The ratio of observed to expected concentrations and the C.V. are plotted against expected concentrations in Figures 4 and 5, respectively. The results indicate relative accuracy within 10% in the range from about 70 to 1400 μg/20 ml. The C.V. values remained constant within 8% over the range 106 to 1418 μg/20 ml.

5. Conclusions

Using AIHL Method 61, both with and without addition of fixed quantities of sulfate, third order regression of the working curve data provides a working range from about 100 to at least 1400 μg sulfate/20 ml. Within this range, the procedure is not improved by the addition of fixed quantities of sulfate to each sample.

Table 7

Relative Accuracy and Precision of AIHL Method 61 $BaSO_4$ Turbidimetric Method (with Sulfate Additions) with an Atmospheric Sample ($\mu g\ SO_4^=/20$ ml Solution)

Concentration, % of Undiluted	Observed Mean of 3 Trials[a]	σ	σ^2	C.V. (%)	Expected Diluted Conc.[b]	Observed Conc. / Expected Conc.
2.5	35.3	8.6	74.4	24.4	35.5	0.995
5.0	71.1	9.2	85.1	13.0	70.9	1.002
7.5	101.7	7.8	61.2	7.7	106.4	0.956
10.0	132.1	6.1	37.4	4.6	141.8	0.931
12.5	163.3	3.6	13.2	2.2	177.3	0.921
15.0	199.2	2.6	6.9	1.3	212.7	0.936
18.75	251.6	6.5	42.1	2.6	265.9	0.946
31.25	426.5	9.5	89.4	2.2	443.2	0.962
43.75	617.4	11.7	137.5	1.9	620.5	0.995
56.25	810.4	10.4	107.8	1.3	797.7	1.016
75.00	1098.8	32.9	1084.8	3.0	1063.7	1.033
100.0	1464.7	29.0	842.5	2.0	1418.2	1.033

Coefficients for Third Order Working Curves

Trial	a	b	c	d	$S_{y.x}$
I	-8.075×10^{-2}	5.621×10^{-4}	1.242×10^{-7}	-2.738×10^{-11}	0.00518
II	-9.096×10^{-2}	5.828×10^{-4}	1.242×10^{-7}	-3.429×10^{-11}	0.0111
III	-6.227×10^{-2}	4.588×10^{-4}	2.476×10^{-7}	-6.555×10^{-11}	0.00485

a. After subtraction of 300 $\mu g\ SO_4^=$.

b. The correct, undiluted concentration was taken from Table 6 to be 1418 ± 49 μg/20 ml solution.

Figure 4
RELATIVE ACCURACY AS A FUNCTION OF SULFATE CONCENTRATION
WITH AIHL METHOD 61 (WITH SULFATE ADDITIONS)
THIRD ORDER REGRESSION FOR THE WORKING CURVE

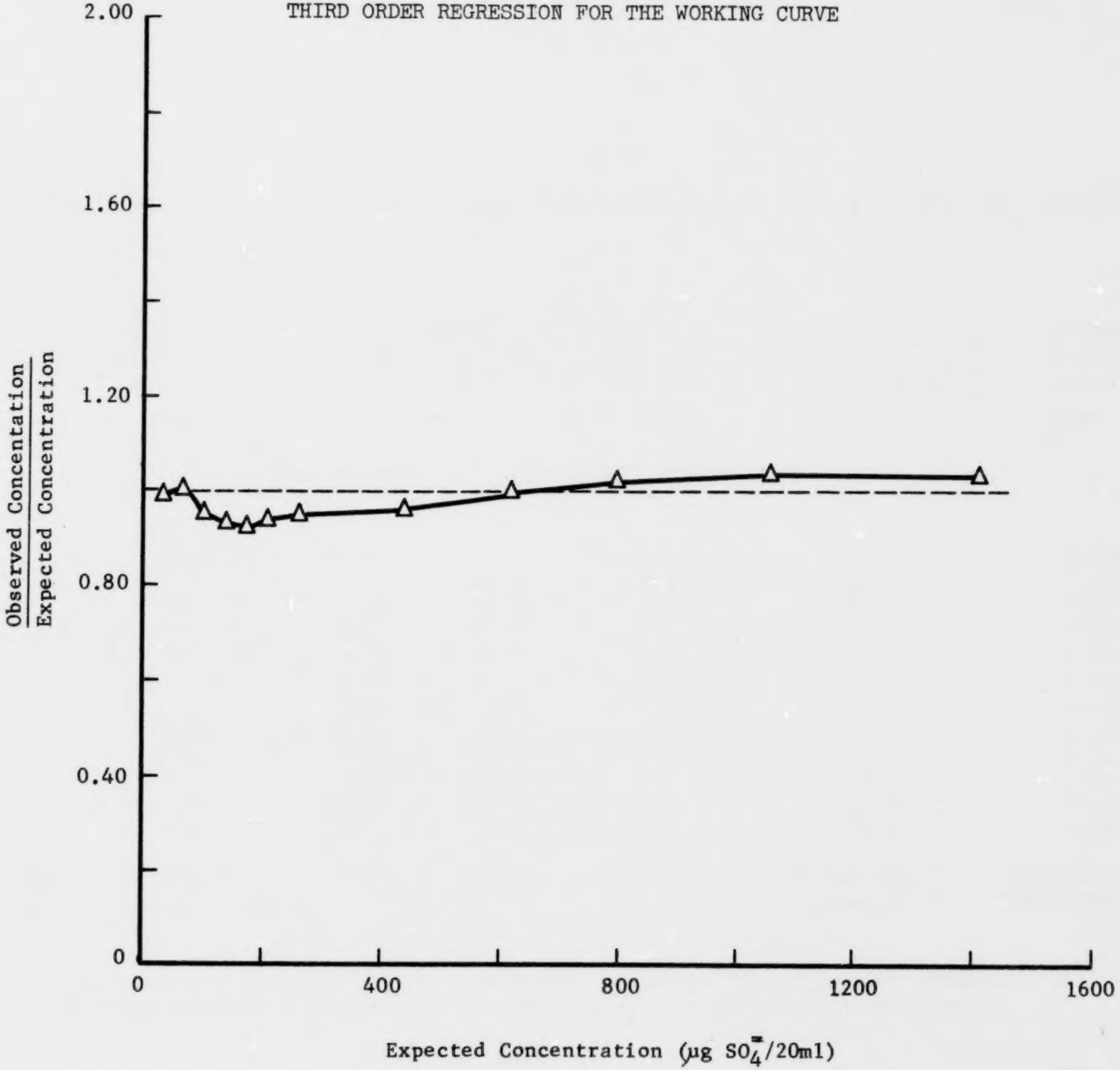
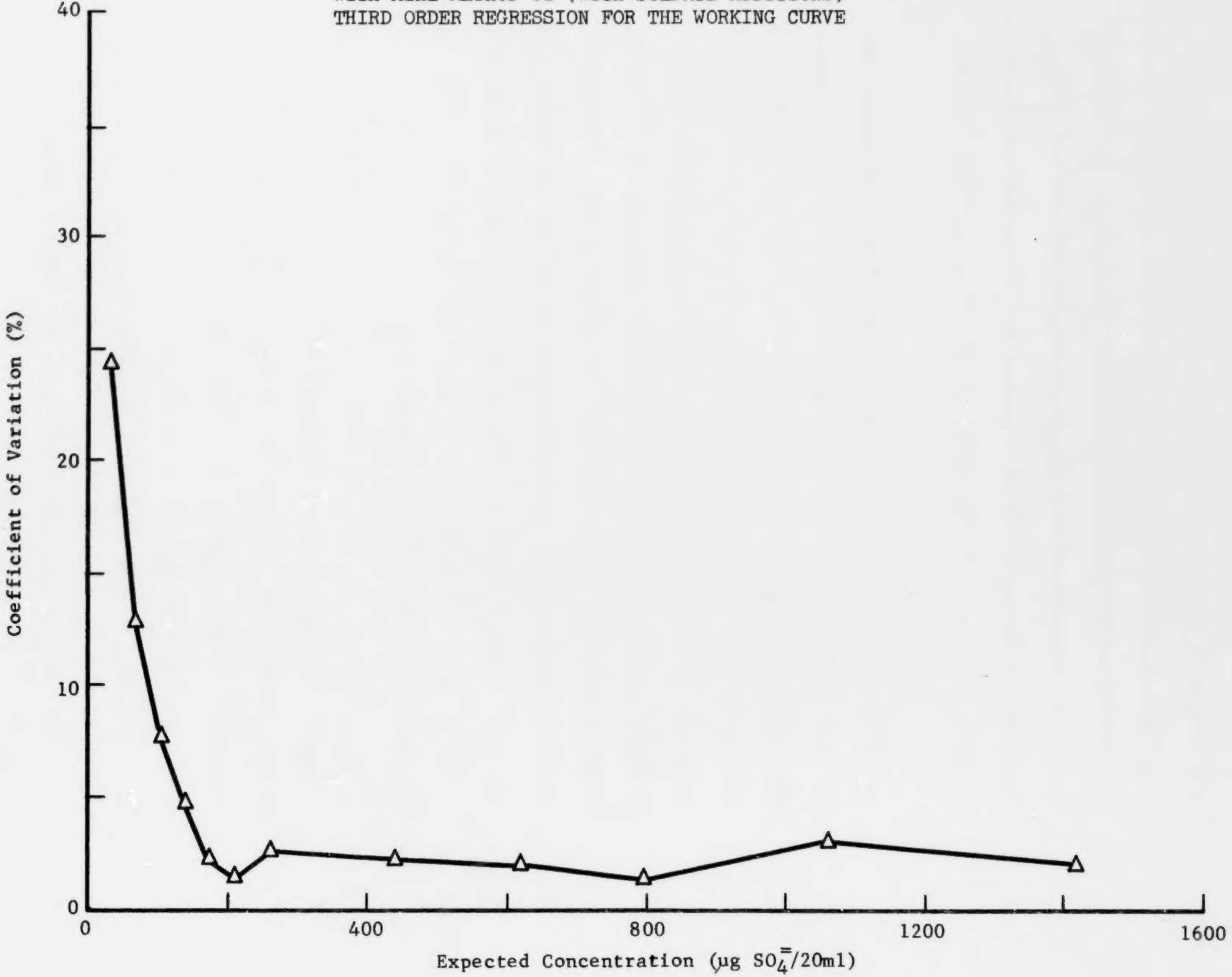


Figure 5

COEFFICIENT OF VARIATION AS A FUNCTION OF SULFATE CONCENTRATION
WITH AIHL METHOD 61 (WITH SULFATE ADDITIONS)
THIRD ORDER REGRESSION FOR THE WORKING CURVE



C. Evaluation of a Modified $BaSO_4$ Turbidimetric Method (AIHL Method 75)

1. Introduction

AIHL Method 61 specifies that 20 ml sulfate samples are mixed with a glycerol-alcohol-acid solution in a graduated cylinder, an aliquot is transferred to a 20 mm diameter cuvet to determine its initial turbidity, then poured back into the graduate and, finally, $BaCl_2$ is added. After agitation and standing for 40 minutes, an aliquot is again transferred to the cuvet and the final turbidity measured.

In the current study, this procedure was modified to eliminate the multiple transfers by mixing the sample and glycerol-alcohol-water and, finally, $BaCl_2$ crystals in inexpensive 25.4 x 150 mm Teflon lined screw capped test tubes also used to determine both initial and final turbidity. Each sample requires a separate test tube. A B&L 20 spectrophotometer was employed since this accepts 25.4 mm diameter glass cells.* The potential advantage of this technique includes reduced chance of contamination and/or loss of samples and increased speed in analysis. This modified procedure is hereafter referred to as AIHL Method 75 or more simply, Method 75. A detailed protocol is included as Appendix B.

2. Evaluation of Working Curves Without Addition of Sulfate

Working curves were prepared, in three trials, covering the concentration range 40-2000 μg sulfate/20 ml. Two curve fitting procedures were evaluated: a log-log fit for the range 40-300 μg/20 ml followed by linear regression in the range 300-2000 μg/20 ml, and, secondly, a third order polynomial fit throughout the range. Figure 6 illustrates the results for one trial. The regression equations and the average goodness of fit by the two procedures as a function of concentration are given in Tables 8 and 9. These results show that (a) below 80 µg/20 ml, curve fitting is poor by third order regression and, below 120 µg/20 ml, relatively poor by log-log fit, (b) the third order fit is superior to the log-log fit + linear regression for the range 40-2000 µg/20 ml sulfate, (c) in the range 300-2000 µg/20 ml, the third order and linear fit differ, in general, by less than 2%, and (d) the log-log (40-260) regression line shows substantial variability from day-to-day in contrast to the linear (300-2000) and third order (40-2000 µg/20 ml) fit.

---

*Test tubes are evaluated for optical matching as described in Appendix B.

3. Accuracy of the Method 75 with Added Sulfate

Three hundred µg of sulfate were added to each of a set of pure sulfate solutions covering the range 40 to 1600 µg/20 ml. The resulting solutions were analyzed by Method 75 using linear regression for working curves in the range 300-1600 µg/20 ml. The mean results for three trials, after subtracting the sulfate added, are compared to the true sulfate values in Table 10.

The results indicate below 300 µg/20 ml an average error of -10.9%. This may be compared to the goodness of fit to the non-linear working curves below 300 µg/20 ml given in Table 9. The mean percent error is substantially lower by either a log-log (average of -0.2%) or third order regression (average of 2.7%). We can infer that for

Figure 6 COMPARISON OF CURVE FITTING PROCEDURES

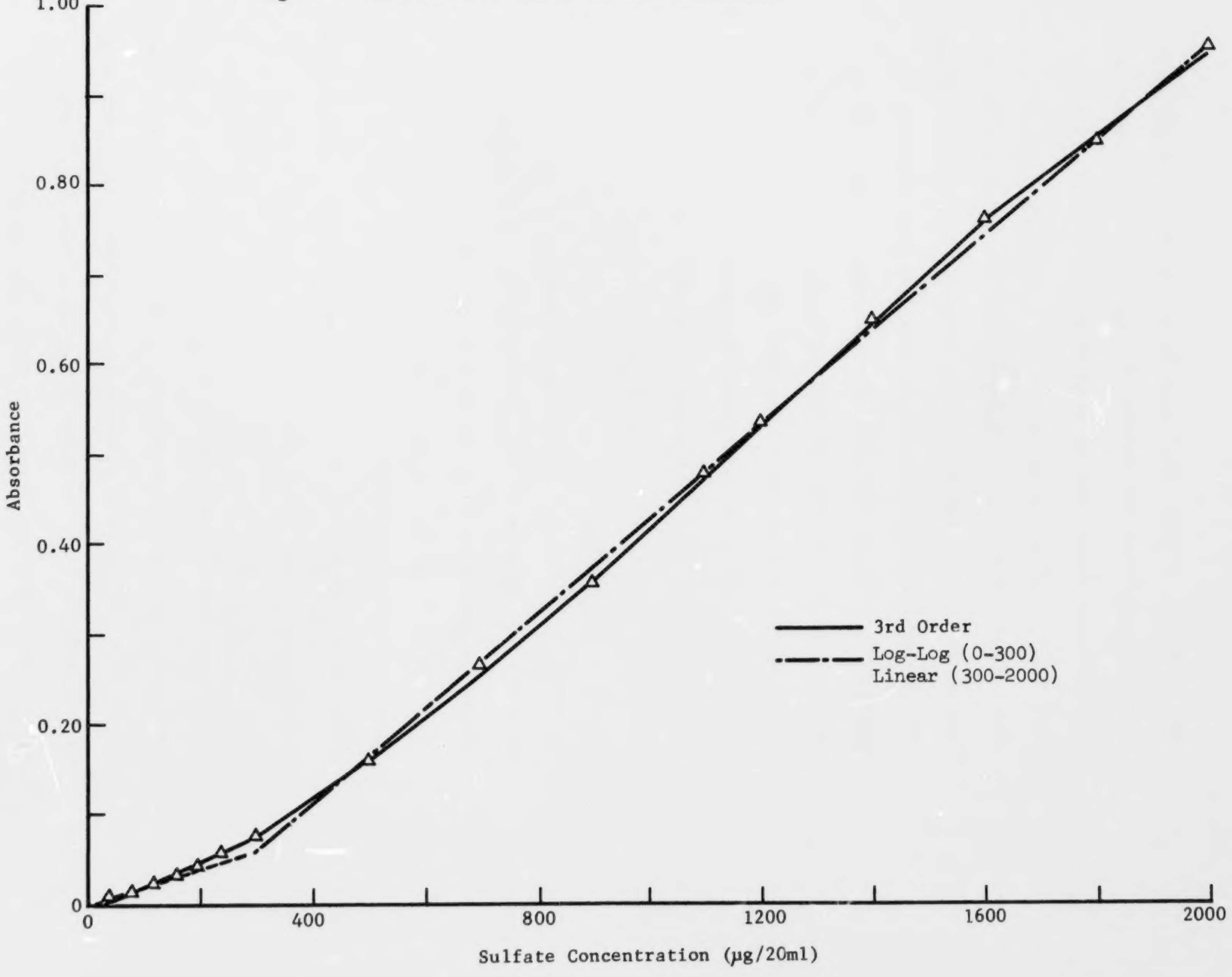


Table 8

Curve Fitting as a Function of Concentration
AIHL Method 75 Without Sulfate Additions
Log-Log and Linear Regression

True Sulfate µg/20 ml	Mean Observed $SO_4^=$	C.V.	Mean Obs. $SO_4^=$ / True Sulfate	Mean % Error
40	42 ± 6.7	16.0	1.05	5.0
80	75.8 ± 15.3	20.2	0.95	- 5.3
120	122.2 ± 5.1	4.2	1.02	1.8
160	152.3 ± 11.7	7.7	0.95	- 4.8
200	208.0 ± 5.0	2.4	1.04	4.0
240	253.7 ± 32.5	12.8	1.06	5.7
300	318.3 ± 9.9	3.1	1.06	6.1
500	484.5 ± 7.3	1.5	0.97	- 3.1
700	671.3 ± 15.4	2.3	0.96	- 4.1
900	883.8 ± 16.8	1.9	0.98	- 1.8
1200	1217 ± 15.8	1.3	1.01	1.4
1400	1420 ± 4.3	0.3	1.01	1.4
1600	1640 ± 37.7	2.3	1.03	2.5
1800	1793 ± 16.1	0.9	1.00	- 0.4
2000	1964 ± 23.6	1.2	0.98	- 1.8

Coefficients for Regression Equations

	For $SO_4^= < 300$ µg/20 ml $(SO_4^=) = a\,(\text{Absorbance})^b$				For $SO_4^= \geq 300$ µg/20 ml $(SO_4^=) = c + d\,(\text{Absorbance})$			
Trial	a	b	r	$S_{y.x}$	c	d	r	$S_{y.x}$
I	0.000327	0.921	0.979	0.0617	-0.0893	0.000528	0.9991	0.0136
II	0.000209	1.01	0.986	0.0552	-0.101	0.000528	0.9994	0.0113
III	0.000013	1.54	0.988	0.0674	-0.0974	0.000543	0.9975	0.0227

Table 9

Curve Fitting as a Function of Concentration
AIHL Method 75 Without Sulfate Additions
Third Order Regression

True Sulfate μg/20 ml	Mean Observed $SO_4^{=}$	C.V.	$\frac{\text{Mean Obs. } SO_4^{=}}{\text{True } SO_4^{=}}$	Mean % Error
40	45.3	79.2	1.13	13.3
80	81.8	5.2	1.02	2.3
120	126.1	4.5	1.05	5.1
160	155.7	6.5	0.97	- 2.7
200	204.6	10.3	1.02	2.3
240	235.7	0.6	0.98	- 1.8
300	283.2	1.0	0.94	- 5.6
500	499.5	0.9	1.00	- 0.1
700	698.6	2.2	1.00	- 0.2
900	902.7	1.3	1.00	0.3
1200	1205	0.5	1.00	0.4
1400	1392	1.0	0.99	- 0.6
1600	1608	2.2	1.01	0.5
1800	1778	1.2	0.99	- 1.2
2000	2016	0.1	1.01	0.8

Coefficients for Regression Equations

$$(SO_4^{=}) = e + fx + g\,x^2 + h\,x^3 \quad \text{for } 40 \le SO_4^{=} \le 2000\ \mu g/ml$$

Trial	e	f	g	h	r	$S_{y.x}$
I	-2.48×10^{-3}	1.78×10^{-4}	3.71×10^{-7}	-1.12×10^{-10}	0.99998	0.00593
II	-2.28×10^{-3}	1.83×10^{-4}	3.30×10^{-7}	-0.922×10^{-10}	0.99999	0.00538
III	2.04×10^{-3}	1.36×10^{-4}	4.42×10^{-7}	-1.36×10^{-10}	0.9998	0.00911

Table 10

Accuracy as a Function of Concentration for the AIHL Method 75 with 300 μg/20 ml Sulfate Addition and Linear Regression[a]

True Sulfate less 300 (μg/20 ml)	Mean Observed $SO_4^{=}$[b] (μg/20 ml)	$\frac{\text{Mean Obs. } SO_4^{=}}{\text{True Sulfate}} \pm \sigma$[c]	Mean % Error[d]
40	41.4	1.036 ± .190	+ 3.5
80	68.5	0.856 ± .039	-14.4
120	101.6	0.846 ± .051	-15.3
160	133.9	0.837 ± .050	-16.3
200	172.4	0.862 ± .023	-13.8
240	217.6	0.907 ± .020	- 9.3
300	264.4	0.881 ± .012	-11.9
500	459.9	0.920 ± .032	- 8.0
700	690.3	0.986 ± .033	- 1.4
900	886.0	0.984 ± .036	- 1.6
1200	1216	1.013 ± .022	+ 1.3
1600	1566	0.979 ± .011	- 2.1

a. A linear regression curve was prepared from 6 points in the range 300-1600 μg/20 ml. An independent set of samples was prepared from sulfate standard solutions covering the range shown. To each sample, 300 μg sulfate were added, the total sulfate determined from the working curve and 300 μg subtracted from the resulting values.

b. Obtained for three independent trials.

c. A precision of ± 1% was estimated for the "true sulfate" concentration to calculate σ values.

d. $\frac{\text{Mean Obs.-True}}{\text{True}} \times 100$

analysis of sulfate below 300 μg/20 ml by AIHL Method 75, at least with pure sulfate solutions, it is preferable to construct a non-linear working curve fit by either a log-log or third order regression technique than to add sufficient sulfate to permit use of the linear portion of the working curve. A more definitive test of the use of addition of standard amounts of sulfate will be given below.

Above 300 μg/20 ml, the sulfate addition procedure yields better accuracy than below this concentration, but the results are still less accurate than without added sulfate (comparing Tables 9 and 10).

The cause of the decreased accuracy (at all levels) is unclear. The Repipet for dispensing the 300 μg $SO_4^=$/10 ml used for the addition of standard amounts of sulfate was calibrated gravimetrically by dispensing sulfate solution. In addition, the repeatability of dispensing this quantity of sulfate was checked by sulfate analysis as part of several experiments. The mean standard deviation for repeatability was 3.6 μg/ml (C.V., 1.2%). The apparent reproducibility of the standard addition from one experiment to another reflects both the repeatability of the Repipet and the uncertainty of the working curve, since each experiment employs a different working curve. Employing linear regression, the observed mean for two experiments (three trials per experiment) was 306.4 ± 13.9 μg/ml (C.V. of 4.5%) which shows that the repeatability of the Repipet, ca. ± 1%, is adequate for the sulfate addition. The reproducibility of the sulfate addition from experiment to experiment

(C.V. = 4.5%) seems to reflect primarily the uncertainty and/or inaccuracy of the regression equation.

4. Working Range of the AIHL Method 75 (without Sulfate Additions)

The results for AIHL Method 75, without addition of standard amounts of sulfate, are compiled in Table 11 employing third order regression of the working curve. The calculated, undiluted concentration of the extract showed no apparent bias between 10 and 100% concentration. Thus, the correct undiluted concentration was taken to be the mean of nine results, 1394 ± 47 μg/20 ml. The ratio of observed to expected concentrations are plotted against expected concentrations in Figure 7. The results indicate accuracy within 7% of the optimal value in the concentration range from 100 to 1400 μg/20 ml. The coefficient of variation of three independent trials is plotted against expected concentration in Figure 8. C.V. values remain less than 6% in the range 140-1400 μg/20 ml.

Thus, based on both relative accuracy and precision (as measured by coefficient of variation), the working range of the modified barium sulfate method, without sulfate additions, is from 140 to, at least, 1400 μg/20 ml using third order regression.

5. Working Range of AIHL Method 75 with Sulfate Addition

The same sample used in Section 3 was analyzed by the AIHL Method 75 turbidimetric procedure after addition of 300 μg sulfate to each sample. Since the data analysis without sulfate additions was done with a third order regression fit for the working curve, the same

Table 11

Relative Accuracy and Precision of the AIHL Method 75 (without Sulfate Additions) with Atmospheric Samples ($\mu g\ SO_4^=/20$ ml solution)[a]

Concentration, % of Undiluted	Observed Mean of 3 Trials	σ	σ^2	C.V. (%)[b]	Calculated Undiluted Concentration	Expected Diluted Concentration[c]	Observed Conc. / Expected Conc.
2.5	55.6	17.5	305.9	50.2	2223.3	34.8	1.595
5.0	84.0	15.5	241.1	22.2	1679.7	69.7	1.205
7.5	111.8	14.5	211.4	13.9	1409.2	104.5	1.069
10.0	141.6	1.5	2.2	1.1	1416.5	139.4	1.016
12.5	177.5	9.8	95.8	5.6	1420.2	174.2	1.019
15.0	197.5	11.0	120.2	5.3	1316.5	209.1	0.945
18.75	248.6	7.4	55.0	2.8	1326.0	261.3	0.951
31.25	426.1	8.2	67.7	1.9	1363.5	435.5	0.978
43.75	623.3	17.0	287.6	2.8	1424.8	609.7	1.022
56.25	787.0	12.5	157.0	1.6	1399.1	784.0	1.004
75.00	1077.6	17.5	305.7	1.7	1436.7	1045.3	1.031
100.0	1440.4	9.1	82.4	0.65	1440.4	1393.7	1.033

Mean undiluted conc. = 1394 ± 47

Coefficients for Third Order Working Curves

Trial	A	B	C	D
I	-7.433×10^{-3}	2.050×10^{-4}	3.506×10^{-7}	-1.110×10^{-10}
II	-1.323×10^{-3}	1.681×10^{-4}	4.026×10^{-7}	-1.366×10^{-10}
III	-2.071×10^{-3}	1.943×10^{-4}	3.334×10^{-7}	-9.603×10^{-11}

a. The samples used were prepared by dilution of the same pooled extract used to evaluate AIHL Method 61

b. $(\sigma/\text{mean}) \times 100$.

c. Equals (Mean undiluted conc.) x (Concentration, % of undiluted) x .01.

Figure [illegible]

RELATIVE ACCURACY AS A FUNCTION OF SULFATE CONCENTRATION
WITH AIHL METHOD 75 (WITHOUT SULFATE ADDITIONS)
THIRD ORDER REGRESSION FOR THE WORKING CURVE

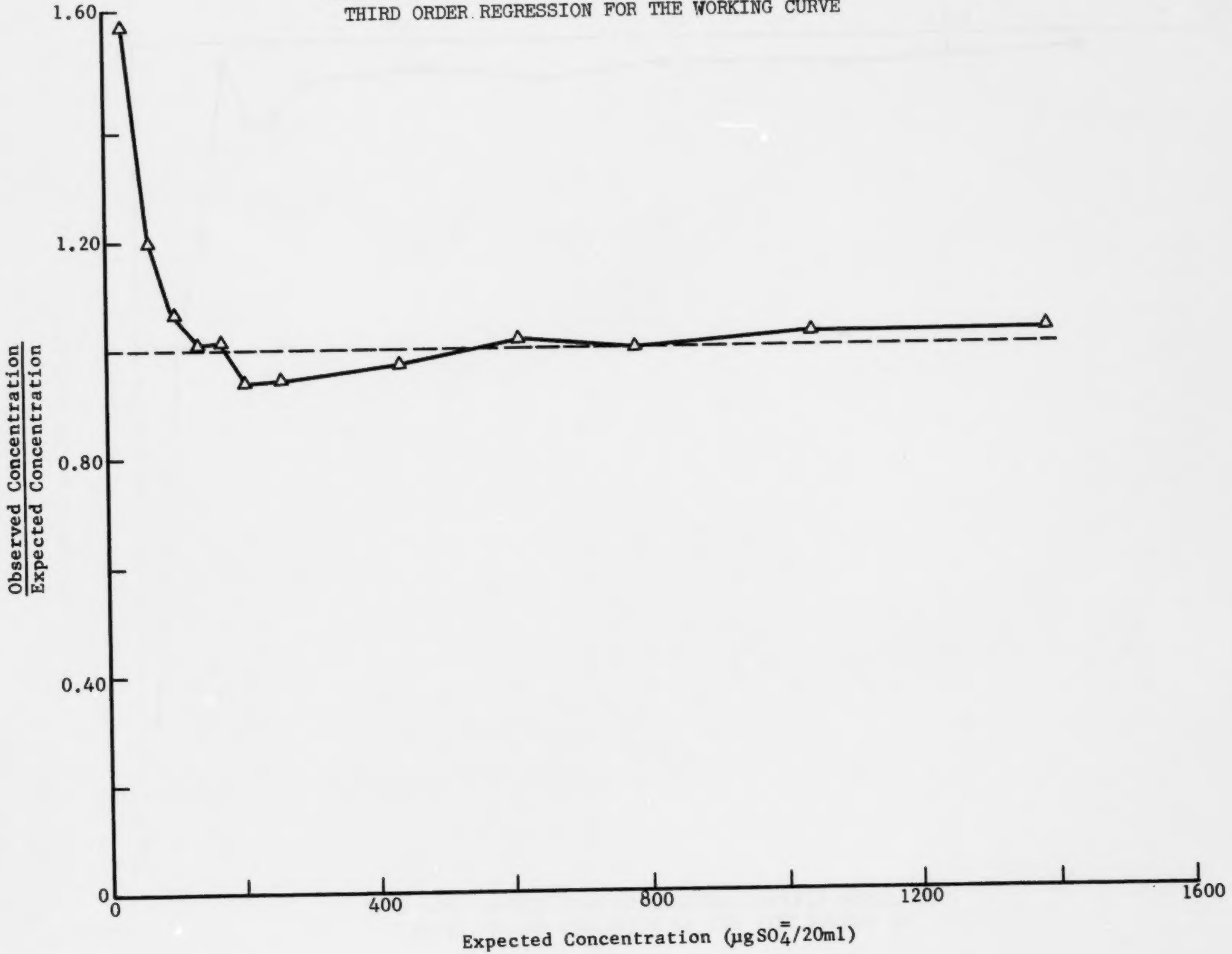
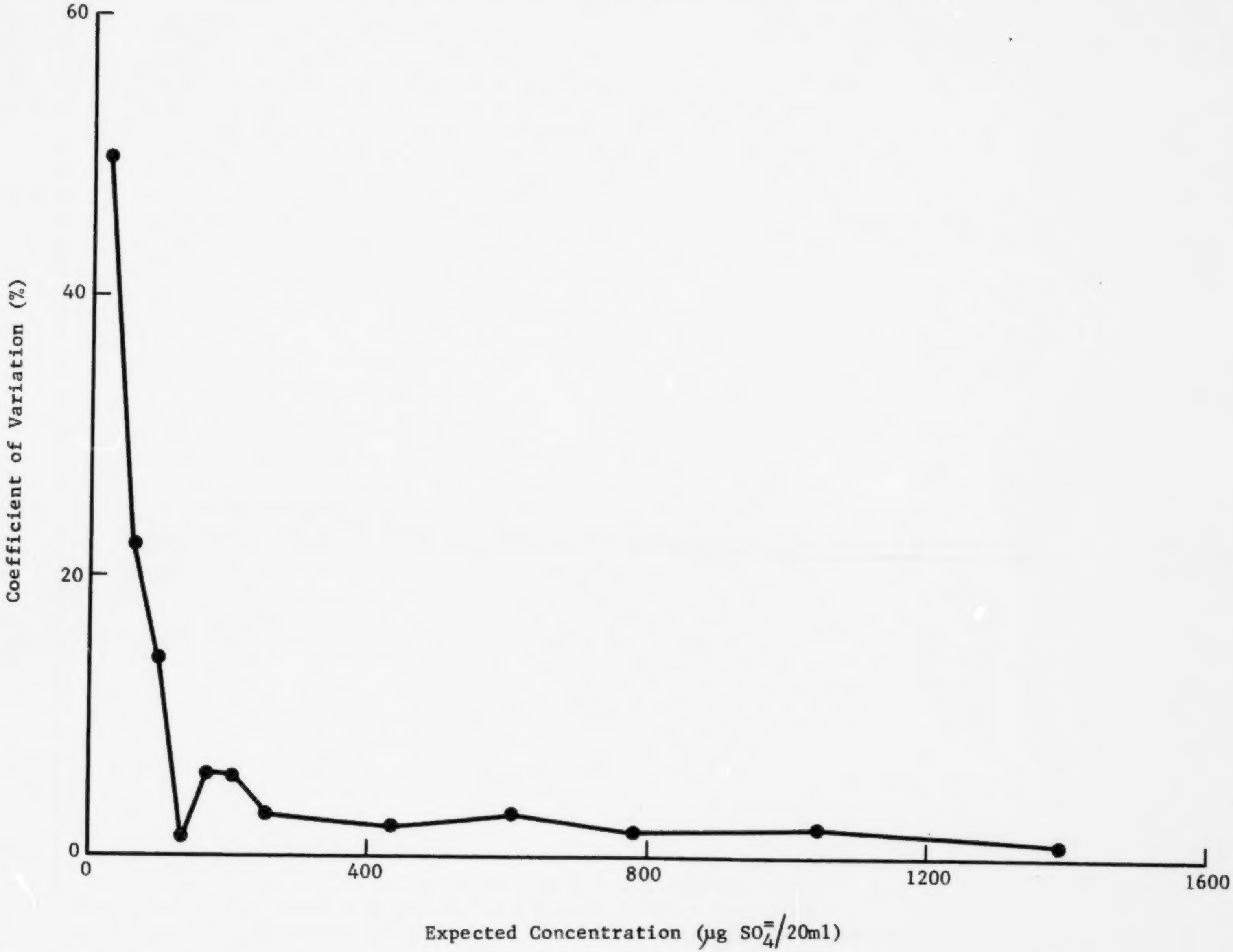


Figure 8

COEFFICIENT OF VARIATION OF THE AIHL METHOD 75
WITH ATMOSPHERIC SAMPLES (WITHOUT SULFATE ADDITIONS)



procedure was used with sulfate additions. The results after subtracting 300 from the observed sulfate, are shown in Table 12. The correct, undiluted sulfate concentration for the atmospheric sample was taken to be 1394 μg/20 ml (Table 4). The ratio of observed to expected concentrations and the coefficient of variation are plotted against expected concentrations in Figures 9 and 10, respectively. The results indicate relative accuracy within 10% in the range from 170 to 1400 μg/20 ml. This is significantly poorer than that found without sulfate additions. C.V. values remained approximately constant from 140 to 1400 μg/10 ml.

The results indicate that the modified method with sulfate addition has a working range from 140 to 1400 μg/20 ml. However, within this range accuracy is significantly inferior to that without addition of sulfate.

6. Accuracy Using EPA Audit Strips

Glass fiber filter strips loaded with five different levels of sulfate, four strips per level,were extracted at room temperature for 30 minute by ultrasonic extraction and filtered through a glass frit. Sulfate analyses by Method 75 are shown in Table 13. The results indicate a fairly consistent positive bias averaging 4% throughout the range. The greatest error, +7%, was found at the lowest solution concentration, 4 μg/ml (80 μg/20 ml).

Table 12

RELATIVE ACCURACY AND PRECISION OF AIHL METHOD 75
(WITH SULFATE ADDITIONS) WITH ATMOSPHERIC SAMPLES (μg $SO_4^=$/20 ml SOLUTION)

Concentration, % of Undiluted	Observed Mean of 3 Trials [a]	σ	σ^2	C.V.(%)	Expected Diluted Conc. [b]	Observed Conc. / Expected Conc.
2.5	27.7	12.1	147.3	43.7	34.8	0.794
5.0	57.1	6.3	39.6	11.0	69.7	0.820
7.5	87.0	6.8	45.8	7.8	104.5	0.832
10.0	118.9	2.9	8.2	2.5	139.4	0.853
12.5	156.8	9.8	96.6	6.3	174.2	0.900
15.0	188.9	6.8	46.1	3.6	209.1	0.904
18.75	238.4	8.0	63.4	3.4	261.3	0.912
31.25	429.3	8.4	71.1	2.0	435.5	0.986
43.75	620.4	29.6	877.4	4.8	609.7	1.02
56.25	823.4	17.5	306.2	2.1	784.0	1.05
75.00	1086.9	45.3	2052	4.2	1045	1.04
100.0	1431.7	24.2	586.3	1.7	1394	1.03

Coefficients for Third Order Working Curves

Trial	A	B	C	D	Sy·x
I	-4.150×10^{-2}	3.364×10^{-4}	1.909×10^{-7}	-5.481×10^{-11}	0.00914
II	-6.060×10^{-2}	4.118×10^{-4}	1.179×10^{-7}	-3.823×10^{-11}	0.00712
III [c]	-7.884×10^{-2}	5.171×10^{-4}	0.521×10^{-7}	-1.904×10^{-11}	0.00791

a. After subtraction of 300 μg $SO_4^=$.

b. The correct, undiluted concentration was taken from Table 4 to be 1394 ± 47 μg/20 ml solution.

c. Employed a new bottle of $BaCl_2$ (sample D as described in Section D).

Figure 9

RELATIVE ACCURACY AS A FUNCTION OF SULFATE CONCENTRATION
WITH AIHL METHOD 75 (WITH SULFATE ADDITIONS)
THIRD ORDER REGRESSION FOR THE WORKING CURVE

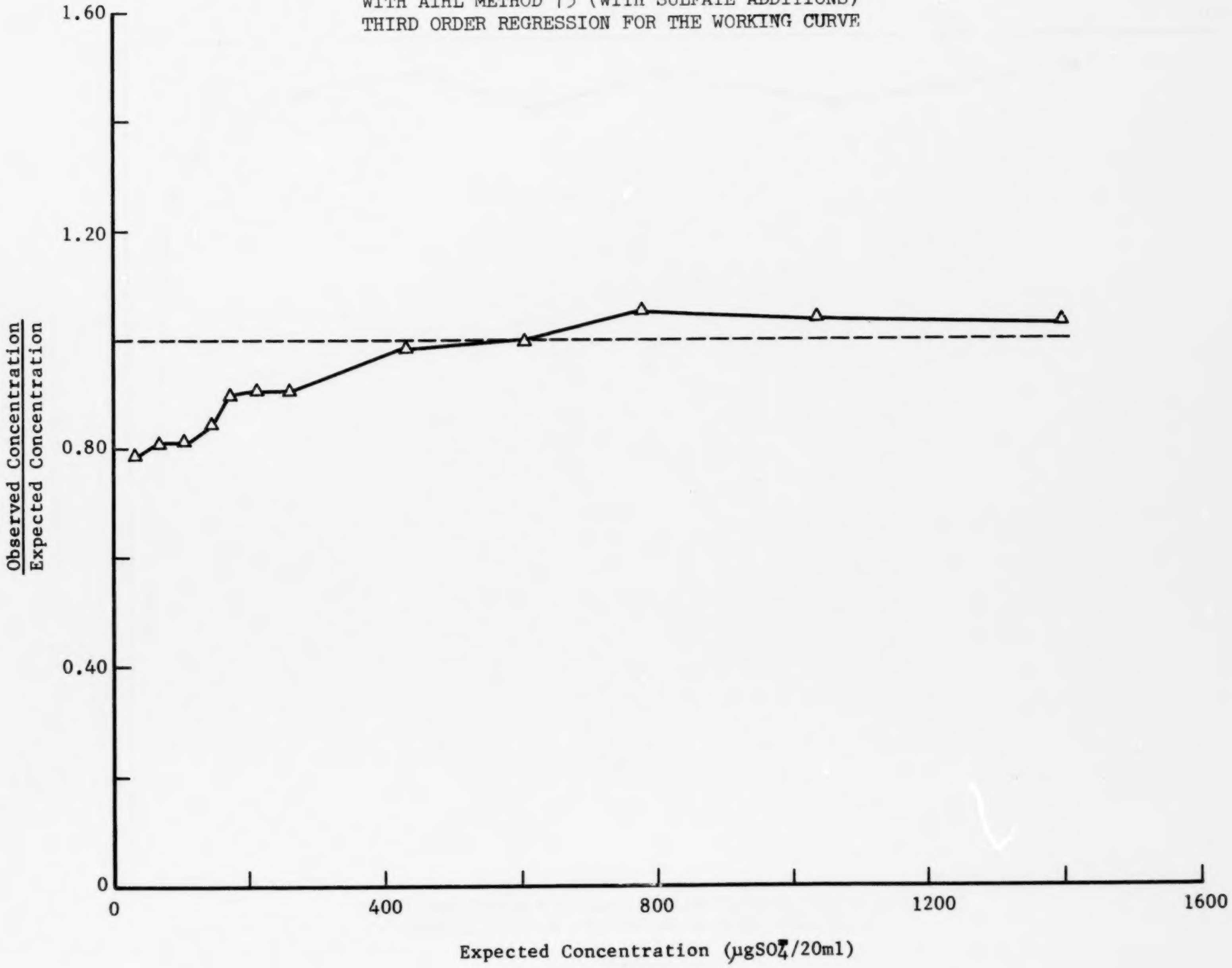


Figure 10

COEFFICIENT OF VARIATION OF AIHL METHOD 75
WITH ATMOSPHERIC SAMPLES (WITH SULFATE ADDITIONS)

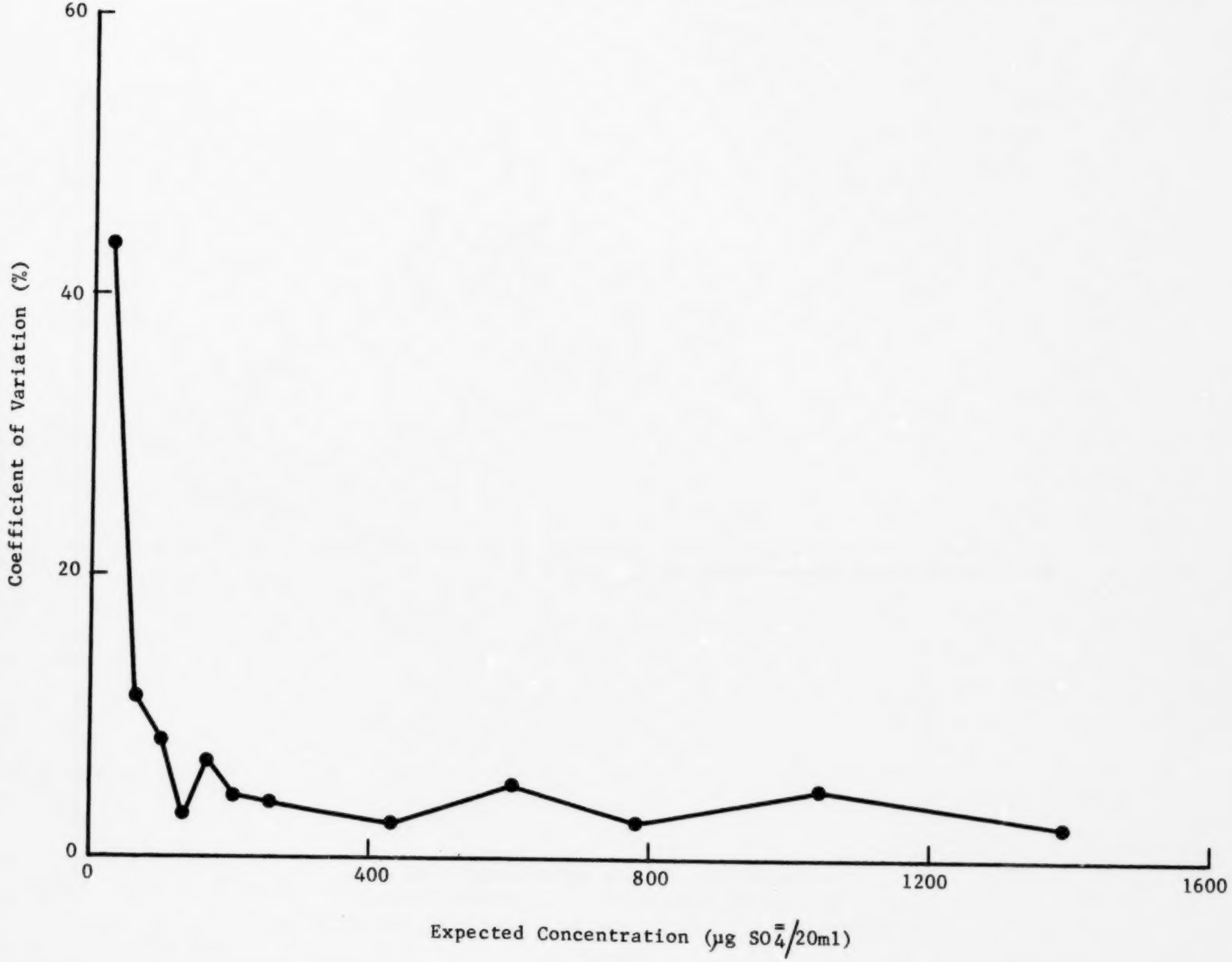


Table 13

ANALYSIS OF EPA SULFATE AUDIT STRIPS BY THE AIHL METHOD 75

Sample	Approximate Concentration Analyzed (μg/ml)	Theoretical Value (μg/strip)	Observed Value (μg/strip)	C.V. (%)	Observed / Theoretical
1000 Series	4	200.2	215 ± 16	7.4	1.07
9000 Series	15	745.6	748 ± 39	5.2	1.00
8000 Series	35	1737.2	1832 ± 11	6.0	1.05
5000 Series	53	2670.1	2812 ± 40	1.4	1.05
7000 Series	85	4240.2	4403 ± 117	2.7	1.04

Regression Equation: $y = -1.26 \times 10^{-2} + 2.70 \times 10^{-4} X + 2.74 \times 10^{-7} X^2 - 9.18 \times 10^{-11} X^3$

$$S_{y.x} = 1.45 \times 10^{-2}$$

$$r = 0.9998$$

7. Conclusions

Using AIHL Method 75 (i.e. the Method 61 version of the barium sulfate turbidimetric procedure modified by carrying out the reaction and reading turbidity values in capped test tubes) with third order regression of the working curve provides a working range from 140 to at least 1400 µg sulfate/20 ml. Method 75 is not improved by the addition of standard quantities of sulfate to each sample. EPA audit strips indicate an accuracy within 6% for samples in the working range.

D. Comparison of Results with AIHL Methods 61 and 75

A summary of results with Methods 61 and 75 is given in Table 14. These results indicate that:

--Method 75 has a slightly narrower working range than Method 61.

--Method 75 is more accurate with standards in the range 80-240 µg/20 ml relative to Method 61. In the 300-2000 µg/20 ml range, the accuracy is about the same.

--For Method 75 with atmospheric samples, relative accuracy is about the same as with Method 61 averaged over the working range. In the range < 300 µg/20 ml, Method 75 is ca. 3% more accurate and 2.4% more precise than Method 61.

Table 14

SUMMARY OF RESULTS OF TURBIDIMETRIC METHODS[a]

	Mean % Error with Standards[b] 80-240	Mean % Error with Standards[b] 300-2000	Working Range	Mean % Error[c]	Mean C.V.(%)	Mean % Error < 300	Mean C.V. < 300 (%)
				Comparisons with Third Order Regression			
AIHL Method 61	6.9	1.8	106-1400	3.3	3.2	- 3.6	5.1
AIHL Method 75	2.6	1.0	140-1400	2.2	2.6	- 1.7	3.7
AIHL Method 61 (with added sulfate)	1.2	1.2	140-1400	4.3	2.3	- 6.7	2.7
AIHL Method 75 (with added sulfate)	9.3	2.3	170-1400	5.5	3.5	- 9.5	4.4
				Comparisons with Linear Regression			
AIHL Method 61	Not feasible	2.9					
AIHL Method 75	Not feasible	2.3					
AIHL Method 61 (with added sulfate)	3.9	1.5					
AIHL Method 75 (with added sulfate)	13.8	4.4					

a. Except as noted, all results were obtained with a pooled atmospheric extract diluted to varying degrees. Concentrations in units of μg $SO_4^=$/20 ml.

b. Results calculated from absolute values of errors to avoid cancellation effect. Error without added sulfate calculated from goodness of fit to working curve.

c. Error relative to that in optimal range of method. Results calculated with absolute values of errors to avoid cancellation effect.

--The addition of fixed amounts of sulfate to Method 75 increases error and decreases precision and working range.

--The addition of fixed amounts of sulfate to Method 61 decreases the error with standards < 300 μg/20 ml but decreases the working range and increases the error with atmospheric samples < 300 μg/20 ml. The precision with atmospheric samples is generally better with added sulfate.

Conclusion: Considering the results in Table 14 and its greater simplicity and speed, the modified turbidimetric method (Method 75) with third order regression and without addition of fixed amounts of sulfate is preferable for analysis of atmospheric samples.

E. Ruggedness Test for Turbidimetric Sulfate Analysis

To obtain additional information on the influence of several variables on turbidimetric procedures for sulfate, a ruggedness test was carried out utilizing the procedures followed in both AIHL Methods 61 and 75. The protocol followed is included as Appendix C.

The factors evaluated are given in Table 15. The results of each of the twelve runs, calculated by third order regression for the working curve, were expressed as the ratio of the observed to the theoretical sulfate level. The effect of each factor was evaluated as the difference between mean results for the runs with high (or plus) and low (or minus) levels. Table 16 ranks the observed effects, squares the effects to

Table 15

FACTORS FOR EVALUATION IN RUGGEDNESS TEST

	Low (-)	High (+)
A = Level of $SO_4^=$	100 μg/10 ml	1000 μg/10 ml
B = Level of Addition of $SO_4^=$	300 μg/10 ml	600 μg/10 ml
C = Age of Reagent Mixture	New (0-1 mo.)	Old (2 years)
D = Varying Strength of Reagent Mixture	(4 ml + 1 ml of 95% ethanol)	5 ml
E = Time After Adding Reagent Mixture Until Mixing	1 min.	10 min.
F = Mixing before Absorbance Reading 1[c,d]	Gentle Mixing[e]	Vigorously for 20 sec.
G = Addition of $BaCl_2$	½ scoop (ca. 0.125 g)	1 scoop (ca. 0.25 g)
H = Mode of Shaking, after Addition of $BaCl_2$	Gently for 45 sec. (1 shake/second)	Vigorously for 45 sec.
I = Timing before Second Absorbance Reading[a]	20 min.	40 min.
J = Spectrophotometer, cell length and mode of mixing[b]	B & L 20, 25.4 mm separate cells	B & L 70, 20 mm graduated cylinder
K = Dummy	-	+

---

a. Following $BaCl_2$

b. Sample and reagents mixed either in separate cells used for turbidity readings or in graduated cylinders with tranfers to a single 20 mm cell for reading turbidity.

c. The absorbance due to initial turbidity of sample plus the glycerin-alcohol-HCl "mixed" reagent before addition of $BaCl_2$.

d. After transfer of solution to cuvet, entrapped bubbles can cause appreciable error in absorbance.

e. Slowly add glycerol-alcohol-acid solution minimizing air entrainment. Mix solution by inverting graduated cylinder slowly (about 2 seconds to invert). After 10 seconds, invert again. Repeat for total 6 inversions.

Table 16

RESULTS OF RUGGEDNESS TEST OF SULFATE ANALYSIS BY TURBIDIMETRY

Factor	Abbreviated Identification	Effect	$(\text{Effect})^2$	$(\text{Effect})^2$ as % of Total
C	Age of reagent	-0.417	0.174	78.8[a]
G	Amount of $BaCl_2$ added	-0.127	0.016	7.3
A	Sulfate level	-0.117	0.0136	6.2
D	Reagent strength	-0.087	0.0075	3.4
E	Wait-time until mixing	0.073	0.0054	2.4
I	Wait-time until A_2	-0.033	0.0011	0.5
H	Shaking mode (after $BaCl_2$)	-0.030	0.0009	0.4
K	Dummy	0.030	0.0009	0.4
F	Shaking mode (before $BaCl_2$)	0.027	0.0007	0.3
J	Spectrophotometer, cells	0.020	0.0004	0.2
B	Sulfate addition	0.013	0.0002	0.1

---

[a] By the procedure of R. A. Stowe and R. P. Mayer, Ind. and Eng. Chem. 58 (2) 36 (1966), only the variance for the age of the reagent exceeds that of the dummy factor at the 95% confidence level.

estimate the variance of the method due to that effect and determine the proportion of the total variance due to each factor.

The results indicate that the age of the pre-mixed reagent (i.e. the solution containing glycerin, water and HCl) is the dominant source of variance in the method. Clearly the shelf life of the pre-mixed reagent is less than two years. Four other factors each contributed > 1% of the total variance, including amount of $BaCl_2$ used, sulfate concentration, reagent concentration and the time following addition of reagent until the solution is mixed. The use of separate cells (i.e. test tubes) for each sample and a different spectrophotometer and cell thickness had a negligible effect on the variance. These changes have been used in the modified $BaSO_4$ method (Method 75) as described in Section III B in an effort to make the procedure simpler and faster.

Further studies are needed on the effect of reagent age to establish the shelf life of the reagent.

F. Influence of $BaCl_2$ Mesh and Crystal Size and Impurities on Sulfate Determination by Turbidimetry

1. Introduction

Literature on $BaSO_4$ turbidimetric methods dating to the mid-1930's[13] as well as published methods[3,14] have generally recommended use of 20-30 mesh $BaCl_2$. This was based on still earlier unpublished studies by Parr.[15] The latter developed an instrument, referred to as the "Parr turbidimeter", for use in determining sulfate in water using barium chloride. While manufacture of this turbidimeter was discontinued about 10 years ago, the only U.S. supplier of $BaCl_2$ crystals for turbidimetric sulfate analysis, J. T. Baker, continued to specify "For Parr Turbidimeter". Recently, Baker has discontinued supplying this grade of $BaCl_2$. Accordingly, an evaluation of alternate grades of $BaCl_2$ was performed.

2. Effects on the Working Curves with Method 75

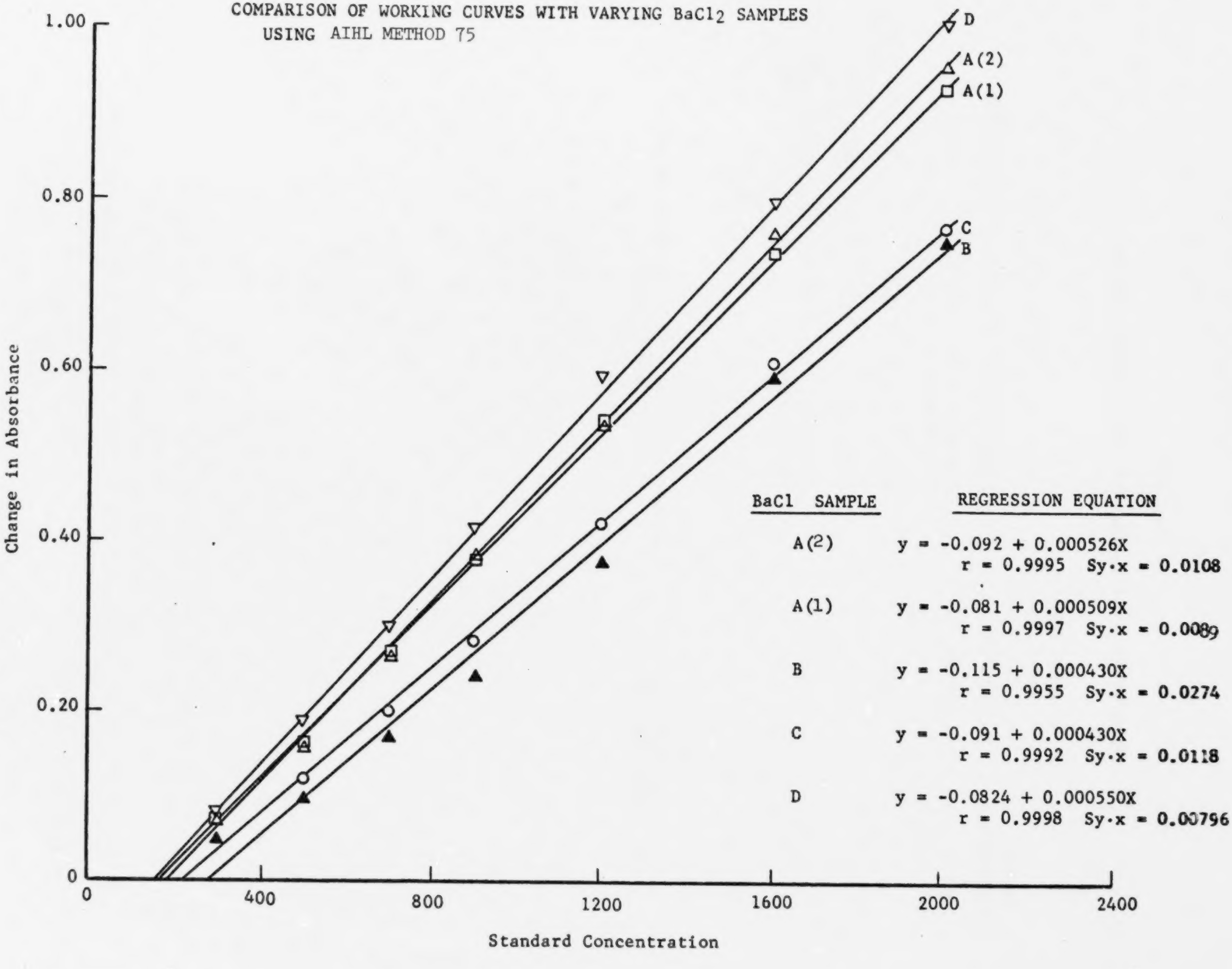
The use of four different sources of $BaCl_2$ (as $BaCl_2 \cdot 2H_2O$) was observed to alter significantly the working curves obtained, in some cases (Figure 11). The four samples are described in Table 17. The studies reported above employed samples A and D. The initial hypothesis adopted to rationalize differences was based on particle size distributions. While sample A had been exhausted, it was labelled "20-30 mesh". The mesh size distribution of the remaining samples was determined.

The results are given in Table 18 together with the mean particle size calculated for each range. Comparison of Table 18 and Figure 11 shows a large difference between working curves for samples B and D consistent with a large difference in mesh size. However samples B and C yielded similar working curves in spite of a comparably large difference in mesh size.

Where sufficient $BaCl_2$ was obtained, the individual size fractions were used to prepare working curves (single trial each) with seven data points between 300 and 2000 μg/20 ml. The results, using

Figure 11

COMPARISON OF WORKING CURVES WITH VARYING $BaCl_2$ SAMPLES USING AIHL METHOD 75



BaCl SAMPLE	REGRESSION EQUATION
A(2)	$y = -0.092 + 0.000526X$ $r = 0.9995$ $Sy{\cdot}x = 0.0108$
A(1)	$y = -0.081 + 0.000509X$ $r = 0.9997$ $Sy{\cdot}x = 0.0089$
B	$y = -0.115 + 0.000430X$ $r = 0.9955$ $Sy{\cdot}x = 0.0274$
C	$y = -0.091 + 0.000430X$ $r = 0.9992$ $Sy{\cdot}x = 0.0118$
D	$y = -0.0824 + 0.000550X$ $r = 0.9998$ $Sy{\cdot}x = 0.00796$

Table 17

DESCRIPTION OF $BaCl_2$ USED FOR TURBIDIMETRIC METHOD

Sample Designation	J. T. Baker Specified Crystal Size (Old U.S. Series Mesh Size)	Stated Purpose	Lot No.	Catalog No.
A	20-30	For Parr Turbidimeter	28793	0974
B	None	None	32561	0970
C	None	None	35371	0970
D	None[a]	For Parr Turbidimeter	528858	1-0974

---

[a] The specifications for this product were quoted as < 5% retained on 20 mesh, < 10% smaller than 70 mesh (i.e., 85% between 20 and 70 mesh).

Table 18

Size Distribution of J. T. Baker $BaCl_2 \cdot 2H_2O$ (% by weight)[c]

Old U.S. Series Mesh Size	Mean Particle Size, μm	Sample B	Sample C	Sample D
≤ 20	1015[a]	50.2	0.4	2.5
20-30	725	13.3	3.4	2.6
30-40	512	11.9	28.7	5.9
40-50	363	7.9	40.2	37.7
50-70	256	5.7	16.6	42.6
> 70	125[b]	10.9	10.8	8.6

a. All particles assumed to be between 16 and 20 mesh (1180 to 850 μm).

b. All particles assumed to be between 400 and 70 mesh (38 to 212 μm).

c. Sieving was done in a particle free hood to minimize contamination using pre-cleaned stainless steel sieves.

linear regression, are given in Table 19. The results suggest that for a given batch the slope increases with increasing $BaCl_2$ particle size. However, sample D shows substantially higher slopes for a given mesh size compared to B and C.

The relation between particle size and slope of the turbidimetric sulfate working curve is shown in Figure 12. If it is assumed that the slope for the working curve observed for the unfractionated samples of $BaCl_2$ is a linear combination of those resulting from the individual size fractions, the slope for the "total sample" can be calculated as:

$$\text{Slope for unfractionated } BaCl_2 = \Sigma\,(px)_i$$

where p = weight percent for fraction i

x = turbidimetric slope for fraction i

Values for x were experimental or were obtained from the regression lines for each sample in Figure 12. A comparison of calculated and observed slopes for the unfractionated $BaCl_2 \cdot 2H_2O$ is given in Table 20. The results indicate agreement within 5%.

These results provide some understanding of factors determining the working curve for a given sample of $BaCl_2$, and help to explain why Batches B and C, which differ so greatly in particle size distribution, can still yield similar slopes. These results left unanswered, however, the source of differences in behavior observed for the same particle sizes from different batches.

Table 19

Working Curves for Method 75 Turbidimetric Method with Size Fractionated $BaCl_2 \cdot 2H_2O$ (Linear Regression)*

Old U.S. Series Mesh Size	Sample B				Sample C				Sample D			
	a	b	r	$S_{y.x}$	a	b	r	$S_{y.x}$	a	b	r	$S_{y.x}$
≤ 20	-.0467	.000469	.9994	.01121	---**	---	---	---	---	---	---	---
20-30	-.0876	.000431	.9986	.01510	-.0841	.000502	.9997	.00877	---	---	---	---
30-40	-.0881	.000407	.9978	.01810	-.0911	.000467	.9991	.01332	---	---	---	---
40-50	-.0909	.000401	.9973	.01982	-.0904	.000448	.9993	.01124	-.0655	.000525	.9990	.01544
50-70	-.0779	.000368	.9971	.01891	-.0891	.000423	.9989	.01338	-.0575	.000508	.9991	.01460
> 70	-.0722	.000388	.9982	.01580	-.0469	.000383	.9971	.01965	---	---	---	---

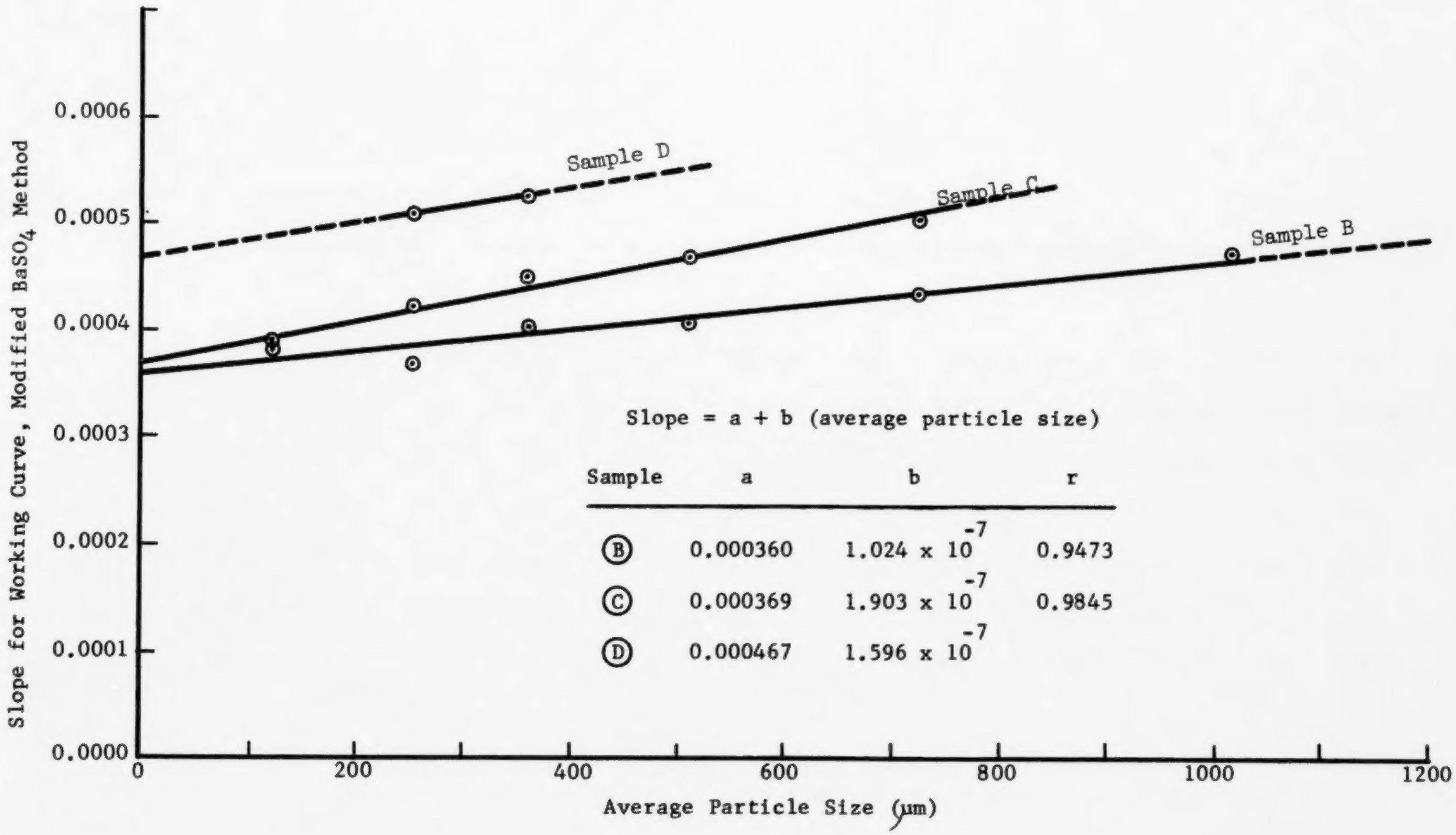
* For ease in data handling, standards were restricted to ≥ 300 μg/20 ml permitting linear regression.

** Dashes indicate insufficient sample for construction of working curve.

Figure 12

THE EFFECT OF $BaCl_2 \cdot 2H_2O$ PARTICLE SIZE ON THE SLOPE FOR THE WORKING CURVE

AIHL METHOD 75



Slope = a + b (average particle size)

Sample	a	b	r
Ⓑ	0.000360	1.024×10^{-7}	0.9473
Ⓒ	0.000369	1.903×10^{-7}	0.9845
Ⓓ	0.000467	1.596×10^{-7}	

Table 20

Comparison of Observed Working Curve Slopes for AIHL Method 75 with those Calculated from Individual Fractions

Sample	Calculated	Observed	Calculated/Observed
B	0.000436	0.000430	1.01
C	0.000445	0.000430	1.03
D	0.000520	0.000550	0.95

G. Impurity Levels in $BaCl_2 \cdot 2H_2O$ Samples

Batches B, C and D were analyzed for Ca, by flame atomic absorption and for Sr and Pb using a heated graphite analyzer. No effort was made to overcome possible interelement interference in these analyses. The results in Table 21, which should be considered approximate, indicate no substantial differences between the samples which might account for the observed differences in the working curves.

H. Dissolving Times for $BaCl_2$ Samples in Water

In an effort to determine the source of the difference in behavior between different batches of barium chloride a simple experiment was performed to compare rates of solution in water. For this purpose one scoop (ca. 0.25 g) of barium chloride of 40-50 mesh size was dropped into 25 ml of distilled water at room temperature in a large test tube (1 inch diameter) being stirred at a standard rate with a small magnetic stirring bar. The time required for dissolving of all crystals was measured with a stopwatch. The results are shown in Table 22 and indicate essentially identical dissolving times for batches B and C while batch D dissolved in approximately half this time. Thus differing rates of solution between D and the other two batches might be related to differences in performance in turbidimetric sulfate analysis.

I. Optical Microscopy of $BaCl_2 \cdot 2H_2O$ Particles

A comparison of the 40-50 mesh fractions was made by optical microscopy scanning over a large number of particles. Photomicrographs considered representative of the samples viewed are shown in Figure 13. The pictures

Table 21

Analysis of $BaCl_2 \cdot 2H_2O$ for Trace Metals (ppm by weight)

Batch	Ca☆	Sr	Pb
B	2 ± 0.5	0.1	0.8
C	1 ± 1	0.05	1
D	1 ± 1	0.05	1.2

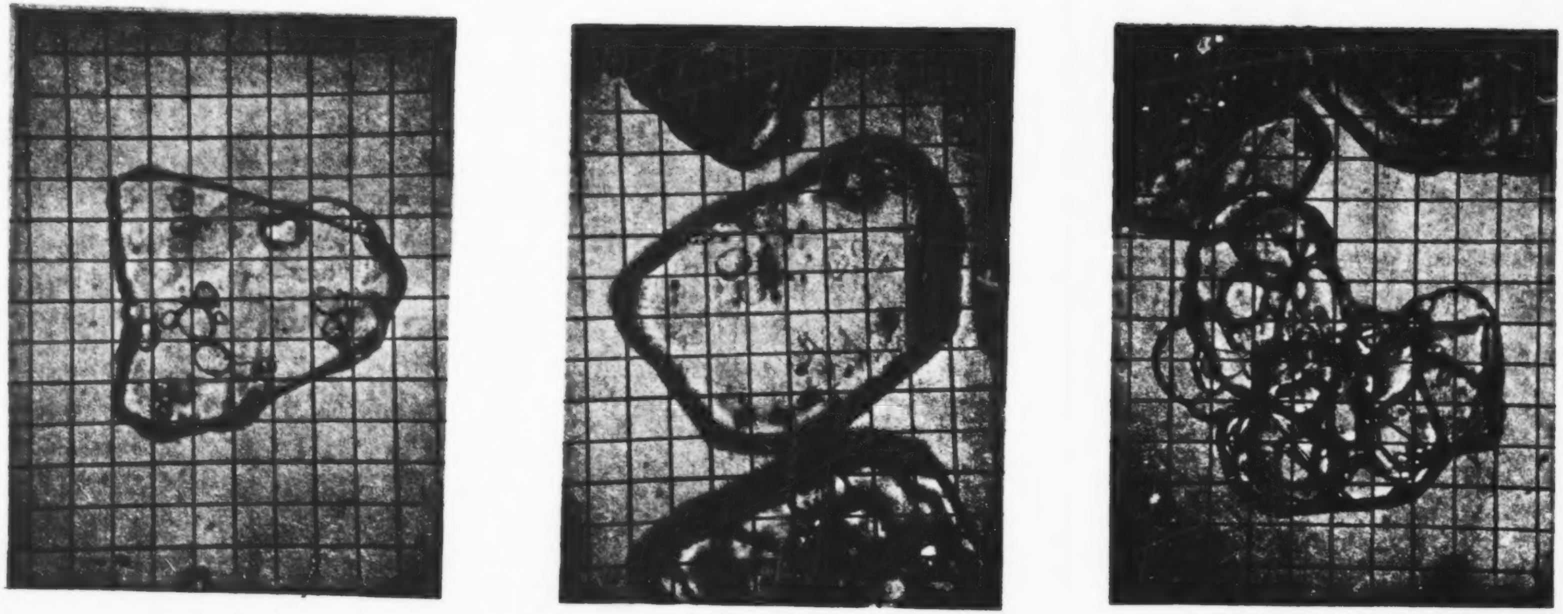
☆All results close to detection limit.

Table 22

Comparison of Dissolving Times for Three Samples of $BaCl_2$

Batch	Time to Dissolve (seconds)[a]
B, 40-50 mesh	35.0
C, 40-50 mesh	35.3 ± 0.4
D, 40-50 mesh	16.5 ± 2.5

a. Mean of two trials ± 1 σ employing 25 ml distilled H_2O at room temperature, constant speed magnetic stirring and 1 scoop (ca. 0.25 g) $BaCl_2$.



$BaCl_2 \cdot 2H_2O$ Sample B
40-50 mesh

$BaCl_2 \cdot 2H_2O$ Sample C
40-50 mesh

$BaCl_2 \cdot 2H_2O$ Sample D
40-50 mesh

Grid Size = 60 μm x 60 μm

Micrographs of Three Samples of 40-50 Mesh Barium Chloride

Figure 13

suggest that for batches B and C the mesh size and the average crystal size are nearly equal. In contrast to these, batch D exhibited a large number of aggregated smaller crystals. The faster rate of solution of batch D is consistent with its smaller average crystal size.

J. Conclusions

The ideal $BaCl_2 \cdot 2H_2O$ batch is one which yields high slopes, small intercepts and little scatter for the working curve. Well size-fractionated particle sizes are not required to achieve good results with the turbidimetric method. For a given batch of $BaCl_2$, its behavior in sulfate analysis is predictable from the properties of its particle size fractions (i.e. crystal aggregate size as obtained by sieving). Working curve slopes increase with increasing crystal aggregate size (or decreasing Old U.S. Series Mesh Size). However, the mesh size is a poor indicator of individual crystal size which, in turn controls dissolution rate. For a given mesh size, smaller crystals, which dissolve faster, yield higher working curve slopes. Thus a coarse mesh size barium chloride (e.g. 20-30 mesh) which consists of aggregates of small crystals appears to be ideal.

IV. EVALUATION OF AN ALTERNATIVE TURBIDIMETRIC TECHNIQUE USING SULFAVER^R

A. Introduction

An evaluation of the use of SulfaVer^R IV* for sulfate analysis of hi-vol extracts was conducted. This material consists of $BaCl_2$ blended with a proprietary colloid-stabilizing material and encapsulated in a plastic pillow-shaped container. One pillow contains the amount required for a single determination. SulfaVer^R is also available in bulk. This evaluation has increased significance because of the current unavailability of crystalline barium chloride graded for use in turbidimetric analyses.

The evaluation included development of an experimental protocol to optimize performance of the method, an evaluation of the accuracy, precision and working range of the method and lastly, an intermethod comparison. The latter will be reported in Section IX.

B. Development of an Experimental Protocol

The method requires addition of the contents of a SulfaVer^R pillow to an aqueous sulfate sample, agitation by some means, allowing the solution to stand for a specified period and reading of the light extinction due to turbidity at 500 nm. Conditions studied are summarized in Table 23. The influence of these conditions on the resulting working curve in the range 100 to 1600 μg/20 ml was evaluated using both linear and third order regression curve fitting procedures.

---

* Hach Chemical Company

Table 23

Conditions Studied in Developing Protocol for SulfaVer^{R}IV Procedure

Agitation (in 25 x 150 mm Teflon-lined screw cap test tubes)	Code
Machine for 60 sec	S_1
Hand (vigorous) 55 sec	S_2
Machine Shaking Speed (oscillations/minute)	
277	s_1
183	s_2
90	s_3
Standing Time Before Reading (min)	
5	w_1
10	w_2
20	w_3
30	w_4
40	w_5
Final Volume (ml)	
20	v_1
25	v_2
Spectrophotometer	
B and L 20 (read in 2.54 cm test tubes)	B_1
B and L 70 (read in 2 cm cuvet)	B_2

Regression curve parameters for each trial are given in Tables 24 and 25 for linear and third order regression, respectively. Trials 1-5 employed a B and L Model 20 spectrophotometer. Since this unit accepts one inch diameter test tubes, turbidity readings were obtained directly in the screw cap test tubes used for mixing the sample and reagent. Trials 6-11 followed a protocol analogous to that in AIHL Method 61: initial turbidity readings were obtained before addition of SulfaVer^R. After addition of SulfaVer^R followed by mechanical shaking in test tubes the samples were transferred to a 2 cm cuvet for reading in a B and L Model 70.

Comparing linear and third order regression, the latter gives a better fit in every case over the range 0 to 1600 µg/20 ml (for linear regression, zero point excluded). From trials 1-5 the minimum in $S_{y \cdot x}$ (third order) for trial 4 was used to select mechanical shaking with 90 oscillations per minute over hand shaking or mechanical shaking at higher speeds. Trials 6-11 employed these conditions but varied waiting time. Trials 7 and 8 were replicates and demonstrated a reproducibility within ± 10% of the working curve. Based on the minimum in $S_{y \cdot x}$ (third order) in Trial 9, a 20 minute wait was chosen. It is clear, however, that the difference in $S_{y \cdot x}$ using 5, 10 and 20 minutes waiting times, is relatively small. A protocol based on this evaluation is included as Appendix D.

The use of the B and L 70 with transfer of samples to a cuvet was chosen to minimize differences from the AIHL Method 61 turbidimetric method. Reading of turbidity directly in the test tubes used for

Table 24

Influence of Protocol Variables on the Working Curve Using SulfaVer^R IV
(Third Order Regression)

Trial	Conditions [a]	a_0	a_1	a_2	a_3	r	$S_{y.x}$
1	S_1, s_1, w_1, v_1, B_1	2.17×10^{-3}	1.86×10^{-4}	9.55×10^{-7}	-3.81×10^{-10}	0.9999	0.96×10^{-2}
2	S_1, s_2, w_1, v_1, B_1	-5.36×10^{-3}	3.68×10^{-4}	6.47×10^{-7}	-2.55×10^{-10}	0.9999	1.10×10^{-2}
3	S_1, s_2, w_1, v_2, B_1	0.40×10^{-3}	0.55×10^{-4}	9.59×10^{-7}	-4.28×10^{-10}	0.9995	1.86×10^{-2}
4	S_1, s_3, w_1, v_1, B_1	-3.54×10^{-3}	2.08×10^{-4}	8.10×10^{-7}	-3.06×10^{-10}	0.9999	0.90×10^{-2}
5	S_2, w_2, v_1, B_1	7.91×10^{-3}	0.13×10^{-4}	1.05×10^{-7}	-3.87×10^{-10}	0.9999	1.42×10^{-2}
6	S_1, s_3, w_1, v_1, B_2	-8.16×10^{-3}	2.93×10^{-4}	6.08×10^{-7}	-1.65×10^{-10}	0.9998	2.13×10^{-2}
7	S_1, s_3, w_2, v_1, B_2	-2.48×10^{-3}	1.92×10^{-4}	8.88×10^{-7}	-2.81×10^{-10}	0.9999	1.06×10^{-2}
8	S_1, s_3, w_2, v_1, B_2	-3.08×10^{-3}	1.85×10^{-4}	8.92×10^{-7}	-2.82×10^{-10}	0.9999	0.99×10^{-2}
9	S_1, s_3, w_3, v_1, B_2	-2.50×10^{-3}	2.37×10^{-4}	7.36×10^{-7}	-2.23×10^{-10}	0.9999	0.72×10^{-2}
10	S_1, s_3, w_4, v_1, B_2	-13.5×10^{-3}	3.72×10^{-4}	4.38×10^{-7}	-0.62×10^{-10}	0.9999	2.03×10^{-2}
11	S_1, s_3, w_5, v_1, B_2	-1.20×10^{-3}	2.16×10^{-4}	7.80×10^{-7}	-2.43×10^{-10}	0.9999	1.19×10^{-2}

---

a. See Table 23

Table 25

Influence of Protocol Variables on the Working Curve Using SulfaVer^R IV
(Linear Regression)

Trial	Conditions[a]	a	b	r	$S_{y.x}$
1	S_1, s_1, w_1, v_1, B_1	-0.83×10^{-1}	8.08×10^{-4}	0.997	3.73×10^{-2}
2	S_1, s_2, w_1, v_1, B_1	-0.69×10^{-1}	8.02×10^{-4}	0.999	2.25×10^{-2}
3	S_1, s_2, w_1, v_2, B_1	-0.81×10^{-1}	6.45×10^{-4}	0.996	2.80×10^{-2}
4	S_1, s_3, w_1, v_1, B_1	-0.93×10^{-1}	7.82×10^{-4}	0.998	2.84×10^{-2}
5	S_2, w_2, v_1, B_1	-1.12×10^{-1}	7.75×10^{-4}	0.995	4.43×10^{-2}
6	S_1, s_3, w_1, v_1, B_2	-1.34×10^{-1}	8.93×10^{-4}	0.996	4.85×10^{-2}
7	S_1, s_3, w_2, v_1, B_2	-1.46×10^{-1}	9.64×10^{-4}	0.997	4.85×10^{-2}
8	S_1, s_3, w_2, v_1, B_2	-1.49×10^{-1}	9.60×10^{-4}	0.996	5.26×10^{-2}
9	S_1, s_3, w_3, v_1, B_2	-1.30×10^{-1}	8.98×10^{-4}	0.996	4.77×10^{-2}
10	S_1, s_3, w_4, v_1, B_2	-1.55×10^{-1}	9.53×10^{-4}	0.993	6.94×10^{-2}
11	S_1, s_3, w_5, v_1, B_2	-1.30×10^{-1}	9.00×10^{-4}	0.996	4.86×10^{-2}

---

a. See Table 23

mixing is a simpler and faster procedure since transfers are avoided; this was set aside for examination of precision and accuracy at a later time with a spectrophotometer which can accept a 25 mm test tube and provide stability and precision at least equivalent to the B and L 70.

Curve fitting as a function of concentration for Trial 9 is shown in Table 26. At 100 μg/20 ml curve fitting is relatively poor by both linear and third order regression. In the range 200 to 1600 μg/20 ml third order regression yields residuals below 2% in all cases.

The reproducibility of the working curve in routine use is illustrated in Figure 14 and Table 27. In four trials, using the protocol given in Appendix D, the greatest variability is observed at the highest concentration.

C. Accuracy with EPA Sulfate Audit Strips

Glass fiber filter strips loaded with five different levels of sulfate, four strips per level, were extracted by ultrasonic agitation in water for 20 minutes, followed by filtration through a glass frit. Sulfate analyses by the SulfaVer^R method are shown in Table 28. The results indicate a positive error of 0 to 10% in the range 15 to 85 μg/ml (300 to 1700 μg/20 ml). The coefficient of variation remained at 6% or less for all samples.

Table 26

Curve Fitting as a Function of Concentration Using a SulfaVer^{R}IV Procedure

True Sulfate µg/20 ml	Linear Regression Mean % Error	3rd Order Regression Mean % Error
100	69.72	-16.46
200	11.74	- 1.92
400	- 9.38	- 0.06
600	-10.16	- 0.41
800	- 4.98	1.18
1200	0.08	-0.52
1600	2.76	0.12

---

a. For Trial 9, Table 25. Mean % error = $\frac{\text{Observed-True}}{\text{True}}$ x 100.

REPRODUCIBILITY OF WORKING CURVE FOR SULFAVER^{R} METHOD

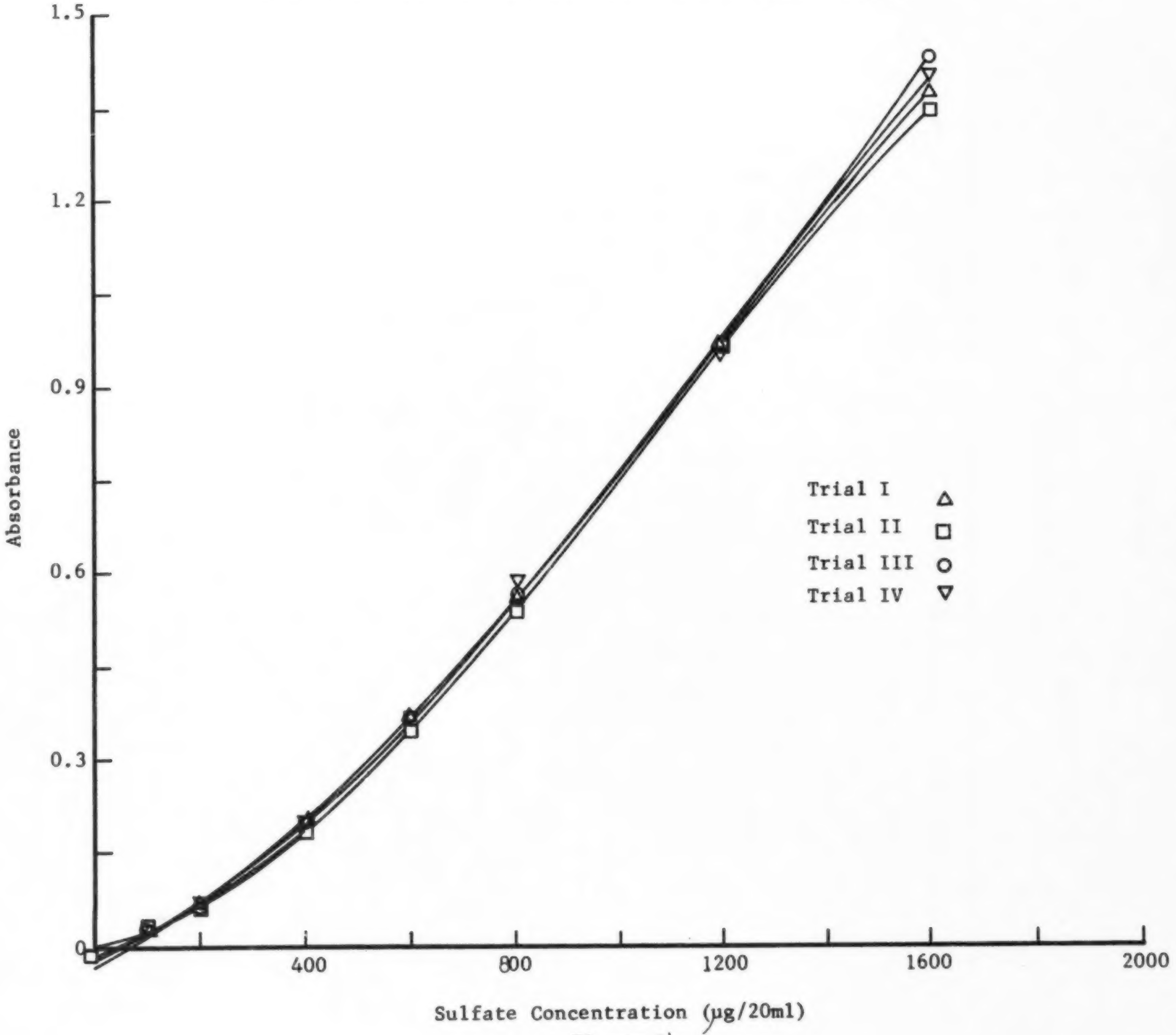


Figure 14

Table 27

Reproducibility of Working Curve for SulfaVer^R Method*
(Third Order Regression)

Trial	a	b	c	d	$S_{y.x}$	r
1	-1.61×10^{-2}	2.84×10^{-4}	7.00×10^{-7}	-2.10×10^{-10}	0.0143	0.9999
2	-0.31×10^{-2}	1.72×10^{-4}	8.44×10^{-7}	-2.65×10^{-10}	0.0035	0.9999
3	-2.33×10^{-2}	3.56×10^{-4}	5.71×10^{-7}	-1.43×10^{-10}	0.0155	0.9999
4	-3.19×10^{-2}	4.21×10^{-4}	4.85×10^{-7}	-1.19×10^{-10}	0.0212	0.9999

---

*Regression equation: $y = a + bx + cx^2 + dx^3$

Table 28

Analysis of EPA Sulfate Audit Strips by a SulfaVer^R Method[a]

Sample	Approximate Concentration Analyzed (μg/ml)	Theoretical Value	Observed Value[b]	C.V.	$\frac{\text{Observed}}{\text{Theoretical}}$
1000 Series	4	200.2	260 ± 16	6.1	1.30
9000 Series	15	745.6	743 ± 43	5.8	1.00
8000 Series	35	1737.2	1905 ± 27	1.4	1.10
5000 Series	53	2670.1	2879 ± 52	1.8	1.08
7000 Series	85	4240.2	4439 ± 243	5.5	1.05

---

a. Results are mean values ± 1 σ for four strips from each series extracted by 30 minutes ultrasonic extraction.

b. Using third order regression data analysis.

D. Working Range

The atmospheric sample extract previously used for evaluating Methods 61 and 75 was diluted to varying degrees to permit evaluation of relative accuracy and precision as a function of concentration. As before, the working range of the sulfate method was considered to be the concentration range which showed both approximately constant relative accuracy and coefficient of variation. The results for the SulfaVer^R method are compiled in Table 29, employing third order regression of the working curve. The calculated, undiluted concentration of the extract showed no apparent bias between 10 and 100% concentration. Thus, the correct undiluted concentration was taken to be the mean of nine results, 1435 ± 47 μg/20 ml. This compares to the values 1394 ± 47 and 1418 ± 49 previously found with the modified $BaSO_4$ method and Method 61, respectively. The ratio of observed to expected concentrations are plotted against expected concentration in Figure 15. The results indicate accuracy within 4% of the optimal value in the concentration range from 143 to 1435 μg/20 ml. The coefficient of variation of three independent trials is plotted against expected concentration in Figure 16. The C.V. values remain less than 6% in the range 180 to 1435 μg/20 ml.

Based on both relative accuracy and precision as measured by coefficient of variation, the working range of the SulfaVer^R method is from about 180 to ≥ 1400 μg/20 ml using third order regression.

Table 29

Relative Accuracy and Precision of SulfaVer^R Turbidimetric Method with an Atmospheric Sample (μg SO_4^{2-}/20 ml)

Concentration, % Undiluted	Observed Mean 3 Trials	σ	σ^2	C.V. %	Calculated Undiluted Concentration	Expected Diluted Concentration	Observed Conc. / Expected Conc.
2.5	51.8	21.8	475.0	42.0	2071.8	35.8	1.445
5.0	93.8	9.6	91.3	10.2	1875.6	71.7	1.308
7.5	117.3	8.8	78.3	7.5	1564.5	107.5	1.091
10.0	142.9	12.7	161.2	8.9	1429.4	143.4	0.997
12.5	171.8	4.5	20.2	2.6	1374.3	179.2	0.959
15.0	204.9	10.6	113.1	5.2	1366.0	215.0	0.953
18.75	258.9	15.1	229.3	5.8	1380.6	268.8	0.963
31.25	456.5	19.5	380.0	4.3	1460.9	448.0	1.019
43.75	647.0	26.4	697.8	4.1	1478.9	627.2	1.032
56.25	830.6	10.7	113.8	1.3	1476.7	806.4	1.030
75.0	1101.6	19.7	387.1	1.8	1468.8	1075.2	1.025
100.0	1466.9	1.4	1.9	0.1	1466.9	1433.6	1.023

Mean undiluted conc. = 1435 ± 47

Coefficients for Third Order Working Curves

Trial	a	b	c	d	$S_{y.x}$	r
I	-1.100×10^{-2}	2.656×10^{-4}	7.598×10^{-7}	-2.409×10^{-10}	8.584×10^{-3}	0.9999
II	-2.084×10^{-2}	2.856×10^{-4}	7.502×10^{-7}	-2.470×10^{-10}	14.1×10^{-3}	0.9999
III	-1.881×10^{-4}	1.209×10^{-4}	9.351×10^{-7}	-2.904×10^{-10}	3.104×10^{-3}	0.9999

RELATIVE ACCURACY AS A FUNCTION OF SULFATE CONCENTRATION
WITH SULFAVER^R (THIRD ORDER REGRESSION FOR THE WORKING CURVE)

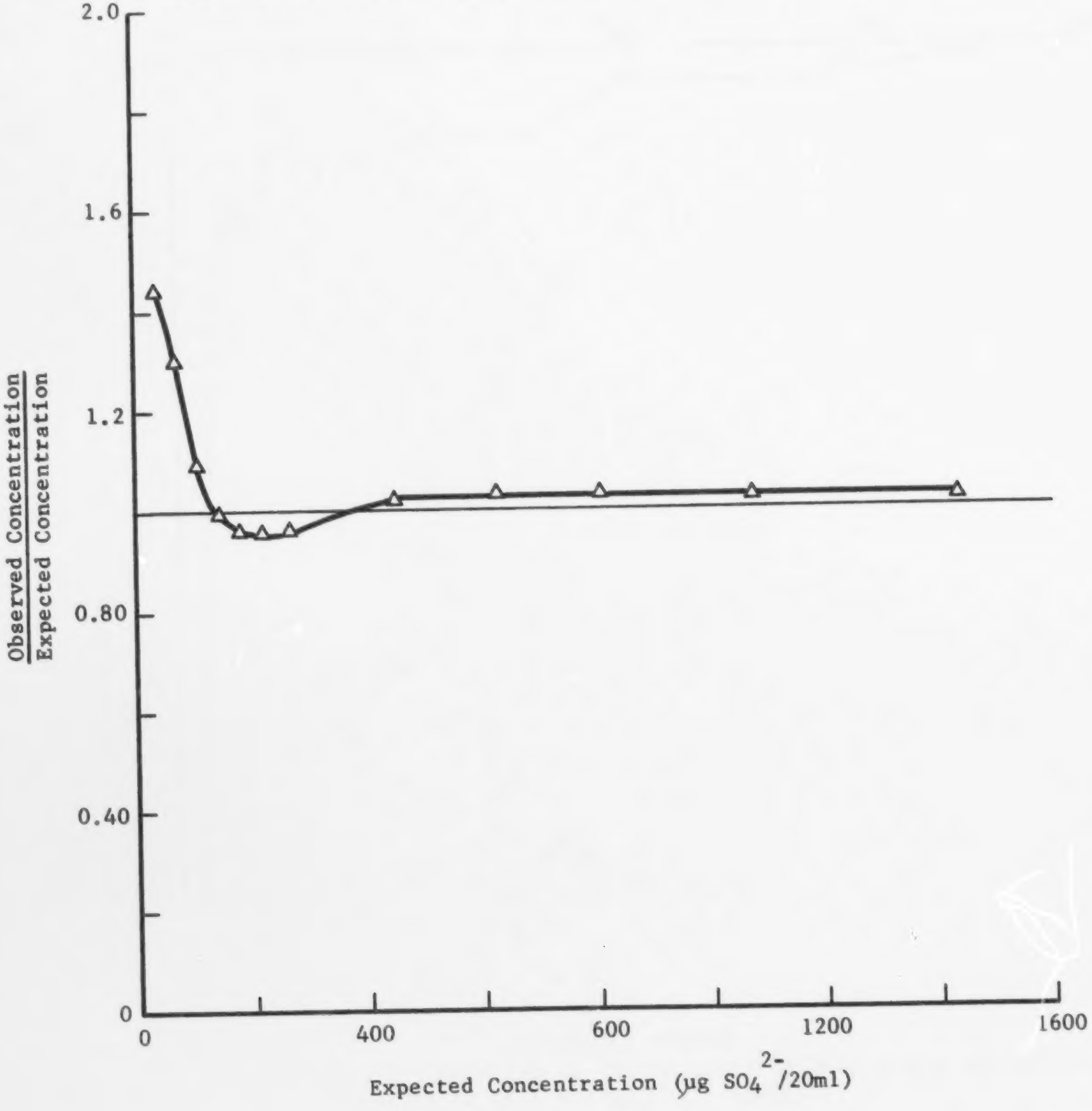


Figure 15

COEFFICIENT OF VARIATION AS A FUNCTION
OF SULFATE CONCENTRATION (THIRD ORDER REGRESSION FOR THE WORKING CURVE)
SULFAVER^R METHOD

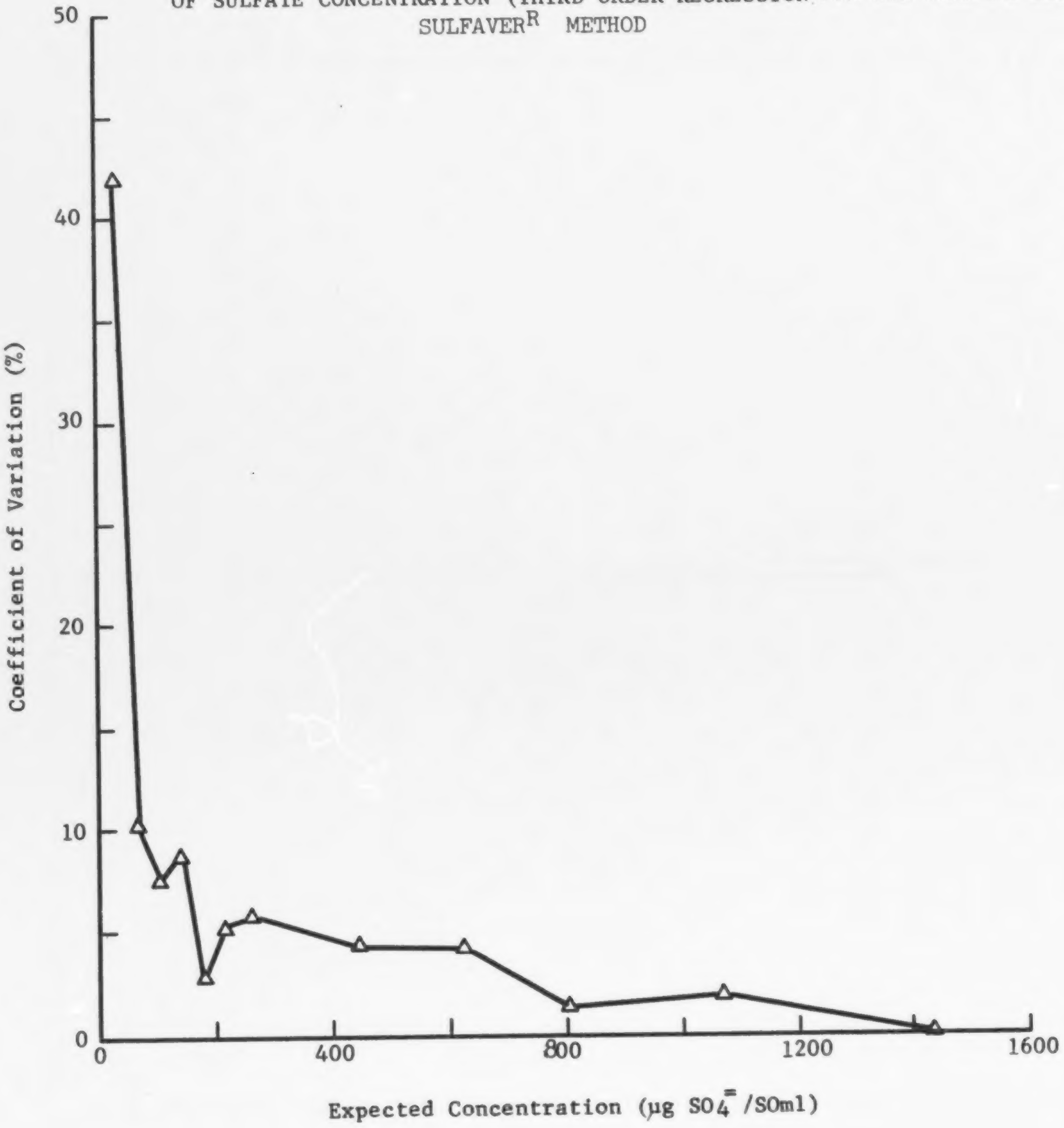


Figure 16

V. EVALUATION OF THE MIDWEST RESEARCH INSTITUTE VERSION OF THE AUTOMATED METHYLTHYMOL BLUE METHOD

A. Introduction

The working curve for the MTB procedure is distinctly non-linear at its extremes. Non-linearity is thought to result from the lack of purity of commercial grades of methylthymol blue.[11] Thus, when a reagent containing 1:1 mole ratio of Ba to MTB is prepared based on an assumed MTB purity of 100%, the resulting reagent, in fact, has a Ba to MTB ratio > 1.0. Because of the formation of a 2:1 Ba-MTB complex with absorbance differing from that of the 1:1 complex, a non-linear working curve results. Accordingly, if the purity of the MTB can be determined, a reagent can be prepared providing known Ba:MTB ratios.

The Technicon was set up according to the MRI method's specifications as detailed in Appendix E, with the following exceptions. A 40 sample per hour timing disc was not initially available so a 30 sample per hour timing disc with a 6:1 sample to wash ratio was installed and used for assaying the MTB. Later studies employed 40 samples per hour as specified. Instead of the linearizer and digitizer (which was not available), a chart recorder was used.

Using 40 samples per hour as specified, the analyses were observed to exhibit a marked memory effect. This was particularly noticeable when successive samples differed greatly in concentration A significant improvement in accuracy and precision was found at lower sample rates (e.g., 30/hour). The memory effect has been eliminated by using two cups for each sample and reading only the second.[2] In spite of the deficiency, the method was evaluated as written (excepting the MTB assay procedure as noted above). Samples were analyzed in random order to provide a realistic measure of the memory effect.

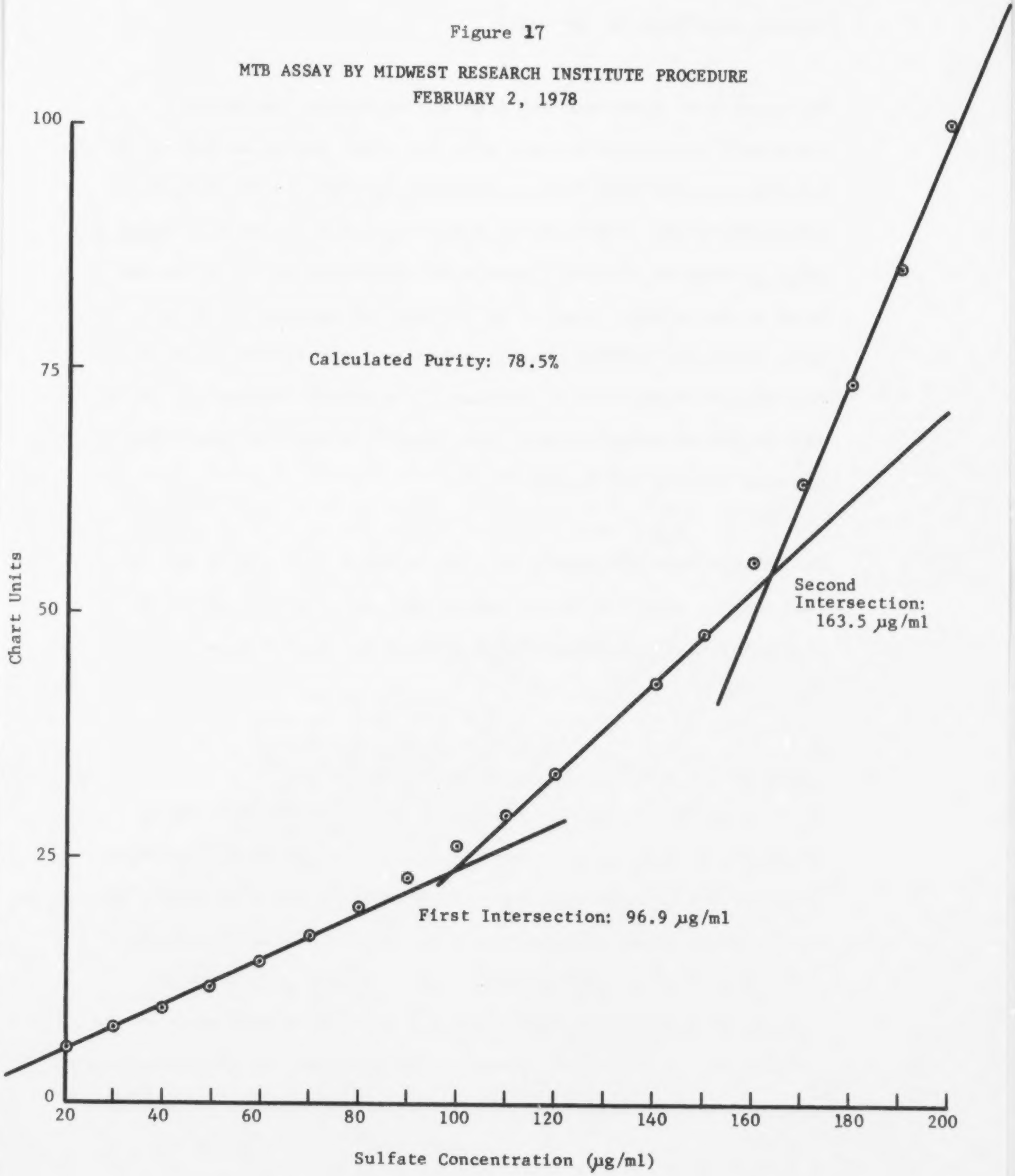
B. Determination of MTB Reagent Purity

The measurement of MTB purity was performed according to MRI's directions using a 3:1 $BaCl_2$ to MTB mole ratio and sulfate standards ranging from 20 to 200 µg/ml. This was replicated on three separate days. During all trials, the baseline remained stable but the span increased despite a one hour or longer warm-up period. This increase was also noted by MRI personnel (F. Bergman, Private Communication, 1978).

When peak height (ordinate) was plotted against sulfate concentration (abscissa), the result in every case was a smooth curve having a continuously increasing slope as illustrated in Figure 17. To measure the purity of the MTB reagent, three straight lines are fit through experimental points of the curve and the intersection points determined. The lines were obtained by selecting points which visually provided the best three linear segments and calculating the respective linear regressions; the intersections were determined mathematically. In the first three trials we experienced the problems of upward drift and of selecting the data points within the three linear regions of the curve. To overcome these difficulties the fourth trial included modifications to the MRI procedure: eighteen (in place of 13) standards were run three times on a given day. The average of these three consecutive runs compensated for the drift and provided more clearly defined linear regions having at least four data points each. (The MRI procedure requires that the standards be run in triplicate

Figure 17

MTB ASSAY BY MIDWEST RESEARCH INSTITUTE PROCEDURE
FEBRUARY 2, 1978



without specifying the protocol).

The first (i.e. lower sulfate) intersection defines the sulfate concentration required to react with the excess barium and the second intersection indicates the concentration required to react with the complexed barium. Purity of the MTB is calculated as shown in Table 30. Table 31 compares the line segments and calculated purity of the MTB found in the trials. Despite the difficulties experienced in the early tests, the Midwest assay procedure was reproducible within 5.5% (coefficient of variation). Because of the greater reliability of the last purity determination made, the value 78.5% was used rather than the mean value of all trials, 74.5%.

The MRI procedure utilizes a ratio of Ba/MTB of 1.13 m/m for MTB of 100% purity. With the current lot of MTB, the weight of impure MTB was increased by the ratio 1/0.785 to provide a Ba/MTB value as specified.

C. Linearity and Reproducibility of the Working Curve

Thirteen sulfate standards ranging from 2 to 100 μg/ml were run in triplicate on three separate days to evaluate the shape and reproducibility of the calibration curve. The graphs obtained consisted of two approximately linear regions, one from 2 to about 30 μg/ml, and the other from 40 to 90 μg/ml (dashed lines in Figure 18). Table 32 compares the correlation coefficient (r) and the standard error of the estimate ($S_{y \cdot x}$) for three options in data handling: 1) linear regression covering the 2-90 μg/ml range, 2) two linear regressions, one for the

Table 30

Calculation of MTB Purity

$$\% \text{ Purity} = \frac{[\mu g\ SO_4^{=}/ml_{(2)} - \mu g\ SO_4^{=}/ml_{(1)}]\ F_1 \times C \times 866.73}{W \times F_2 \times 2} \times 100$$

where:

$\mu g\ SO_4^{=}/ml_{(2)}$ = µg/ml reading from second intersection point

$\mu g\ SO_4^{=}/ml_{(1)}$ = µg/ml reading from first intersectors point

F_1 = flow rate in ml/min for sample line (normally 0.32)

C = molar concentration of stock solution (normally 1.041×10^{-2})

866.73 = molecular weight of MTB

W = weight of MTB in mg

F_2 = flow rate in ml/min for MTB line (normally 0.7)

2 = value to calculate MTB concentration on basis of equivalents/liter

Calculation of Weight of MTB

$$\text{Weight of material for analysis} = \frac{0.164 \times 100}{\% \text{ Purity}}$$

Table 31

Assay of MTB by Midwest Research Institute Method[a,b]

Trial	Line 1		Line 2		Line 3		Purity, %
	a	b	a	b	a	b	
1	1.80	0.246	-13.03	0.400	-125.98	1.13	68.9
2	-1.42	0.253	-18.93	0.443	-133.7	1.17	76.2
3	-0.79	0.272	-16.17	0.435	-117.7	1.10	74.4
4	0.60	0.232	-22.27	0.468	-147.5	1.23	78.5
Mean Slope:	0.251 ± .017		0.437 ± .028		1.16 ± .06		
					Mean Purity:		74.5 ± 4.1

a. Eastman Kodak methylthymol blue, Lot No. E3X

b. Intercept = a, Slope = b

Figure 18

WORKING CURVE FOR MRI-MTB PROCEDURE
FEBRUARY 27, 1978

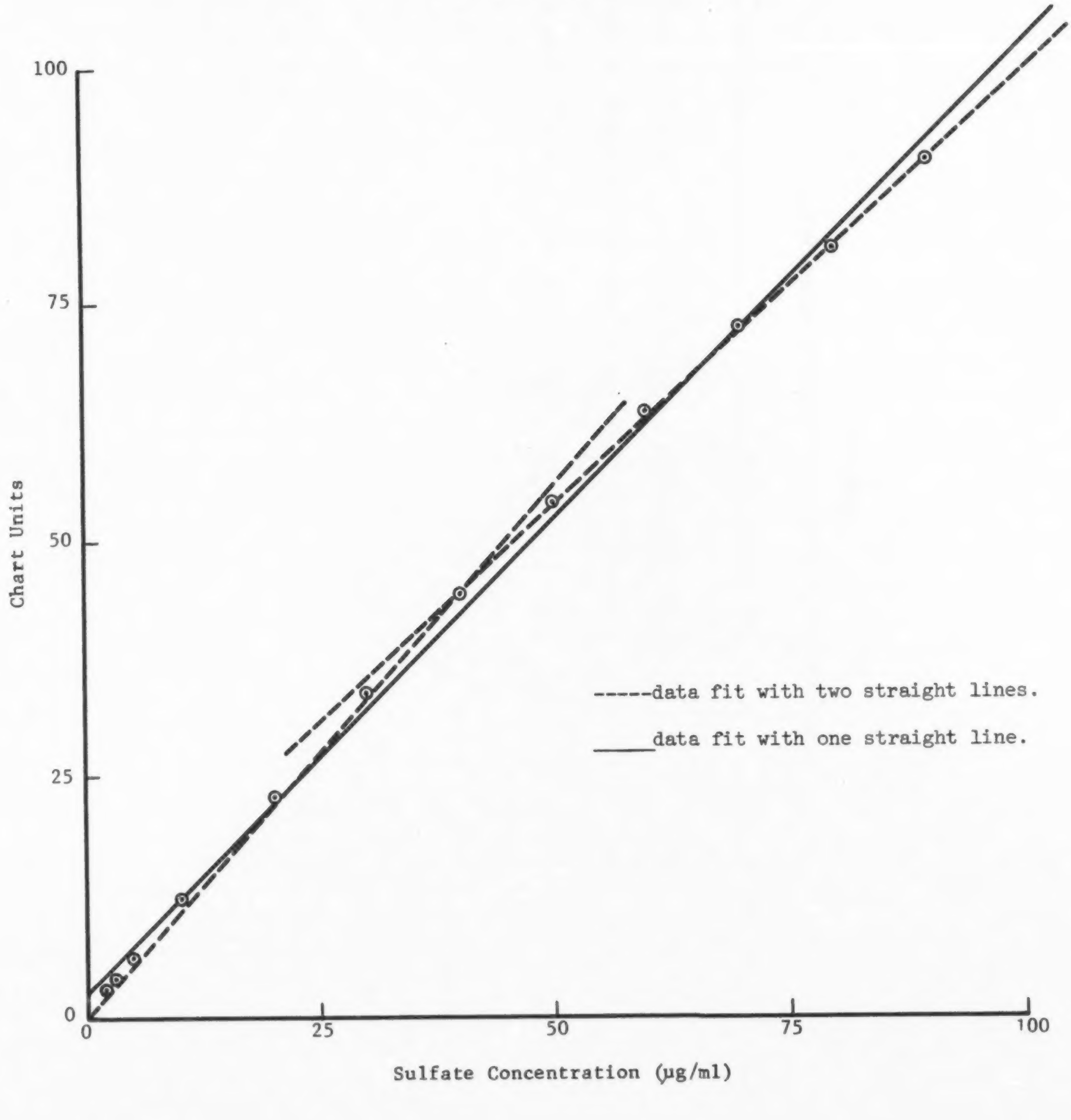


Table 32

REPRODUCIBILITY OF CALIBRATION: SULFATE BY MRI-MTB METHOD

Trial	One Straight Line				Two Straight Lines					Third Order+					
	a*	b**	r	$S_{y.x}$	Range	a	b	r	$S_{y.x}$	a	b	c	d	r	$S_{y.x}$
1	1.77	1.01	0.9988	1.47	2-30	0.24	1.12	0.9996	0.358	-0.12	1.2	$-2.9\cdot10^{-3}$	$6.5\cdot10^{-6}$	0.9999	0.386
					40-90	7.90	0.92	0.9993	0.598						
2	3.44	0.98	0.9967	2.46	2-30	1.36	1.13	0.9868	2.01	0.95	1.2	$-3.5\cdot10^{-3}$	$8.1\cdot10^{-6}$	0.9999	1.78
					40-90	10.0	0.89	0.9942	1.72						
3	2.66	1.04	0.9985	1.72	2-30	1.13	1.14	0.9995	0.354	0.98	1.2	$-0.4\cdot10^{-3}$	$-0.14\cdot10^{-6}$	0.9999	0.535
					40-90	9.78	0.93	0.9975	1.07						

---

*a = intercept

**b = slope

+$y = a + bx + cx^2 + dx^3$

2-30 and the other for the 40-90 μg/ml range, and 3) third order regression for the 2-90 μg/ml range. This comparison based on working curves constructed on three separate days, confirms the presence of two approximately linear regions, with reproducible slopes, but third order regression over the entire range gives a slightly superior fit, as measured by $S_{y.x}$.

The goodness of fit of the three regression techniques as a function of concentration is illustrated for a single trial in Table 33. Fitting a single line in the range 2-100 μg/ml yielded large errors at low concentrations. The difference between the two straight line fit and third order regression was not significant.

An experiment was performed to evaluate the effect of a 5% error in the MTB assay on the working curve since a 5% C.V. was found for the assay. The calibration standards were run using a reagent with a 5% excess MTB in one case and a 5% deficiency in the second. Table 34 shows that neither the slope nor the shape of the curve are affected.

D. Accuracy with EPA Sulfate Audit Strips

Glass fiber filter strips loaded with five different levels of sulfate, four strips per level, were extracted following the MRI 30 minutes ultrasonic extraction procedure. Sulfate analyses by the MRI-MTB method are shown in Table 35. The results indicate a positive error of 9 and 14% at 15 and 4 μg/ml, respectively, using third order regression. At higher concentrations, the error remains $\leq$ 4%. Except at 4 μg/ml, the coefficients of variation remained at or below 5%.

Table 33

CURVE FITTING AS A FUNCTION OF CONCENTRATION FOR THE MRI-MTB METHOD

Sulfate Standard (μg/ml)	% Error		
	Single Straight Line	Third Order	Two Straight Lines
100	-7.5	-1.6	-4.2
90	-2.9	+1.2	-0.9
70	-0.7	+0.3	-0.4
50	+4.0	+2.0	+0.8
30	+5.7	+1.7	0
20	+5.6	+2.2	+2.1
10	+1.3	+5.0	+5.0
5	-23.1	+0.3	-3.0
3	-43.0	+6.3	-3.3
2	-71.3	+11.3	-6.3

Table 34

EFFECT OF A 5% ERROR IN MTB ASSAY UPON THE CALIBRATION CURVE FOR THE MRI-MTB METHOD

Error	One Straight Line				Two Straight Lines					Third Order+					
	a*	b**	r	$S_{y.x}$	Range	a	b	r	$S_{y.x}$	a	b	c	d	r	$S_{y.x}$
+5%	1.77	1.00	0.9985	1.64	2-30 40-90	0.02 8.05	1.12 0.91	0.9991 0.9983	0.495 0.946	-0.19	1.2	$-1.5 \cdot 10^{-3}$	$-5.0 \cdot 10^{-6}$	0.9999	0.595
-5%	2.23	1.01	0.9988	1.52	2-30 40-90	0.74 8.75	1.11 0.92	0.9997 0.9992	0.290 0.654	0.62	1.1	$-0.75 \cdot 10^{-3}$	$-9.6 \cdot 10^{-6}$	0.9999	0.270

---

*a = intercept

**b = slope

+$y = a + bx + cx^2 + dx^3$

Table 35

ANALYSIS OF EPA SULFATE AUDIT STRIPS BY THE MRI-MTB METHOD[a]

Sample	Approximate Concentration Analyzed (μg/ml)	μg/strip Theoretical Value	μg/strip Single Line Regression	μg/strip Two Line Regression	μg/strip Third Order Regression	C.V. (Third Order Regression)	Third Order Theoretical
1000 Series	4	200.2	182 ± 53	233 ± 49	229 ± 40	17	1.14
9000 Series	15	745.6	812 ± 36	837 ± 32	810 ± 43	5.3	1.09
8000 Series	35	1737.2	1894 ± 80	1874 ± 75	1780 ± 84	4.7	1.03
5000 Series	53	2670.1	2829 ± 35	2549 ± 79	2666 ± 39	1.5	0.999
7000 Series	85	4240.2	4261 ± 57	4393 ± 61	4406 ± 92	2.1	1.04

---

a. Results are mean values ± 1 σ for four strips from each series extracted by 30 minutes ultrasonic extraction.

E. Working Range

The concentrated atmospheric sample extract previously used for evaluating turbidimetric methods was diluted to varying degrees to permit evaluation of relative accuracy and precision as a function of concentration. Because the working curve in the 0-100 μg/ml range only approximated a straight line, the data was analyzed both by linear and third order regression. The results are given in Table 36 and Table 37. The calculated, undiluted concentration of the extract showed no bias in both cases at 12.5% and higher concentration. Thus the correct undiluted concentration was taken to be the mean of eight results 139 ± 4.5 μg/ml (linear regression) or 137 ± 3.6 μg/ml (third order). These compare to 139 ± 4.7 μg/ml by the AIHL Method 75 and 142 ± 4.9 μg/ml by AIHL Method 61.

The ratios of observed to expected concentrations are plotted against expected concentration in Figure 19. The results indicate accuracy within 7% of the optimal value in the concentration range from 17 to 91 μg/ml using linear regression. With third order regression, accuracy at low sulfate concentrations is significantly better compared to linear regression. In the range 17 to 89 μg/ml the results are within 5% of the optimal value. The coefficients of variation of three trials are plotted against concentration in Figure 20. Little difference in precision is noted between linear and third order regression except for samples < 5 μg/ml. The C.V. values are < 4% by both linear and third order regression in the range 10-90 μg/ml.

Based on both relative accuracy and precision as measured by C.V., the working range of the MRI-MTB method is from 17 to ≥ 90 μg/ml by both

Table 36

Relative Accuracy and Precision of MRI-MTB Method with an Atmospheric Sample (μg $SO_4^{=}$/ml)

Linear Regression

Concentration % of Undiluted	Observed Mean of 3 Trials	σ	C.V.(%)	Calculated Undiluted Concentration	Expected Diluted Concentration	Observed Conc. / Expected Conc.
2.5	2.7	0.23	8.8	106.4	3.5	0.764
5.0	5.0	0.32	6.3	100.5	7.0	0.722
7.5	8.5	0.28	3.3	113.5	10.4	0.815
10.0	12.1	0.39	3.2	121.3	13.9	0.872
12.5	16.7	0.45	2.7	133.6	17.4	0.960
15.0	20.5	0.43	2.1	136.4	20.9	0.980
18.75	27.9	0.73	2.6	148.6	26.1	1.067
22.0	31.0	0.17	0.6	141.0	30.6	1.013
31.25	43.9	0.10	0.2	140.6	43.5	1.010
43.75	60.6	0.50	0.8	138.5	60.9	0.995
56.25	77.6	0.41	0.5	138.0	78.3	0.992
65.0	89.1	0.10	0.1	137.1	90.5	0.985

Mean undiluted = 139 ± 4.5

Coefficients for Linear Regression Working Curves

Trial	a	b	$S_{y.x}$
I	1.75	0.978	1.983
II	2.29	0.978	1.786
III	0.311	1.000	2.002

Table 37

Relative Accuracy and Precision of MRI-MTB Method with an Atmospheric Sample (μg $SO_4^=$/ml)

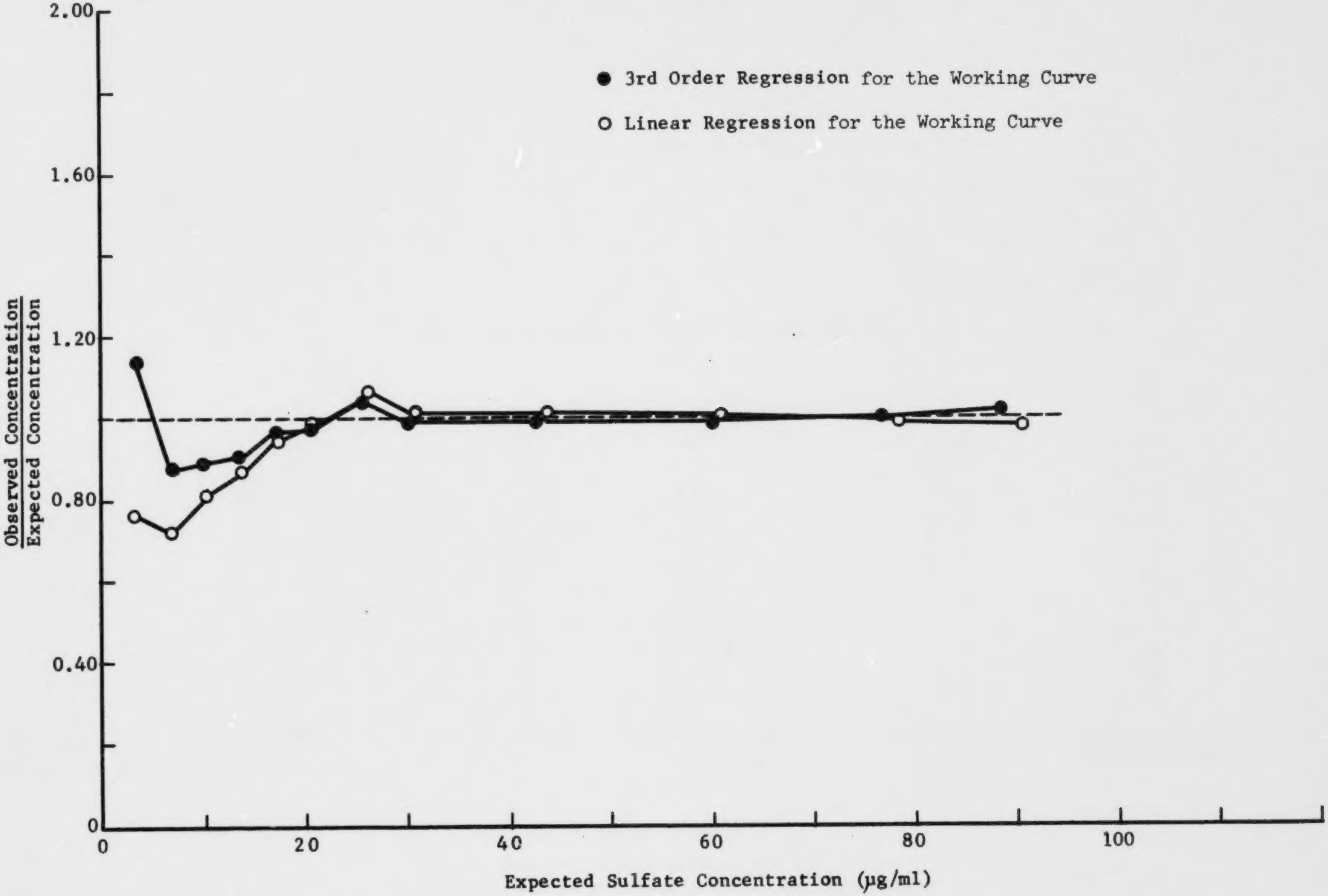
Third Order Regression

Concentration % of Undiluted	Observed Mean of 3 Trials	σ	C.V.(%)	Calculated Undiluted Concentration	Expected Diluted Concentration	Observed Conc. / Expected Conc.
2.5	3.9	0.14	3.5	156.0	3.4	1.140
5.0	6.0	0.35	5.8	120.4	6.8	0.880
7.5	9.2	0.22	2.4	122.3	10.3	0.894
10.0	12.5	0.34	2.7	124.5	13.7	0.910
12.5	16.6	0.42	2.6	132.9	17.1	0.971
15.0	20.1	0.33	1.7	133.8	20.5	0.978
18.75	26.9	0.65	2.4	143.7	25.7	1.050
22.0	29.9	0.29	1.0	135.9	30.1	0.994
31.25	42.3	0.29	0.7	135.4	42.8	0.989
43.75	59.1	0.72	1.2	135.0	59.9	0.986
56.25	77.5	0.41	0.5	137.9	77.0	1.007
65.0	91.1	0.06	0.1	140.2	88.9	1.025

Mean undiluted = 137 ± 3.6

Coefficients for Third Order Working Curves

Trial	a	b	c	d	$S_{y.x}$
I	1.105×10^{-1}	1.092	-3.297×10^{-4}	-1.073×10^{-5}	1.431
II	7.536×10^{-1}	1.084	-5.894×10^{-4}	-0.670×10^{-5}	1.381
III	-15.429×10^{-1}	1.135	-10.144×10^{-4}	-0.545×10^{-5}	1.480



RELATIVE ACCURACY AS A FUNCTION OF CONCENTRATION FOR THE MRI-MTB METHOD

Figure 19

COEFFICIENT OF VARIATION AS A FUNCTION OF CONCENTRATION FOR THE MRI-MTB METHOD

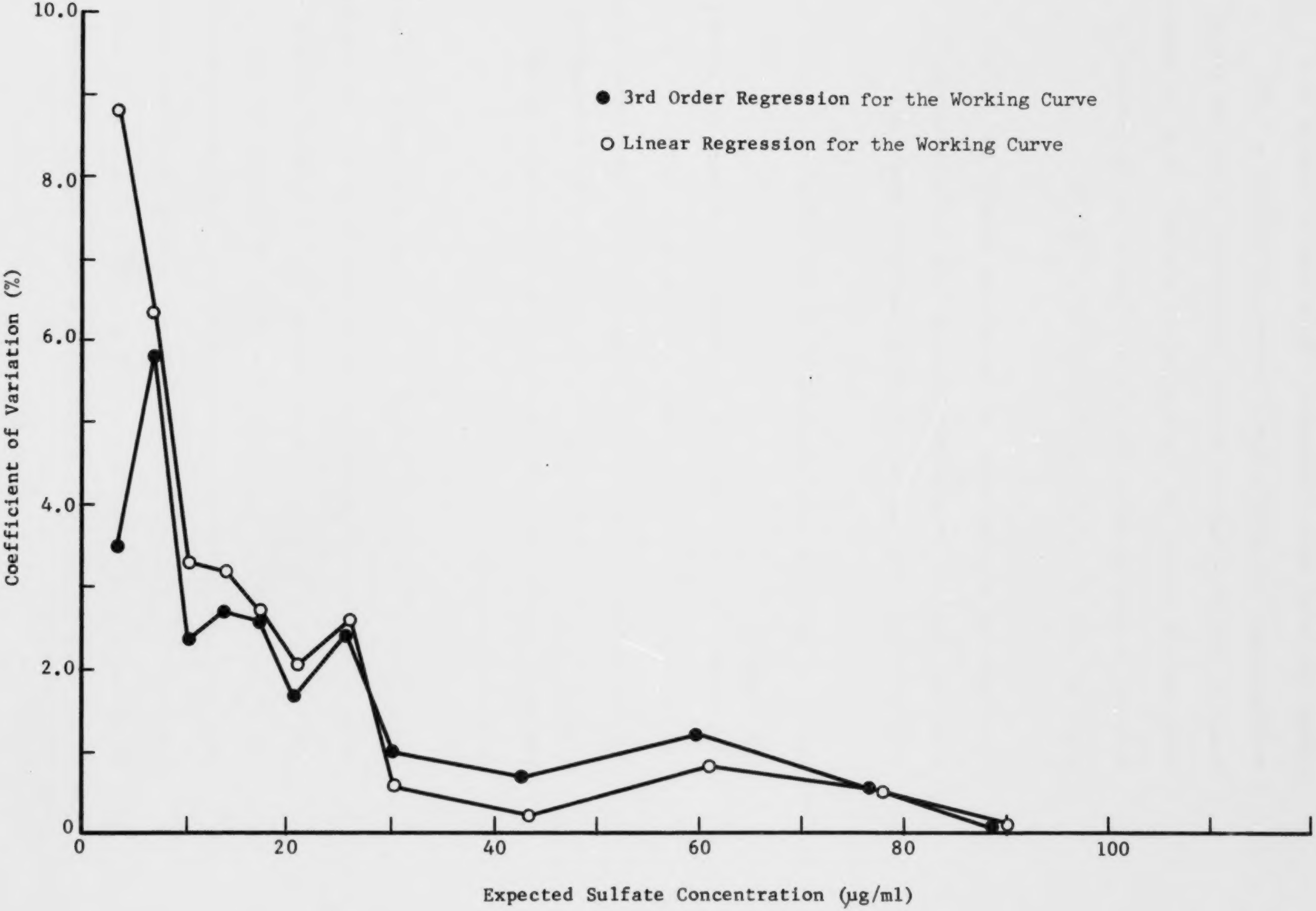


Figure 20

linear and third order regression. These results compare to a working range 7-75 μg/ml (linear regression, accuracy ± 5.5%) found by this procedure for another modification of the MTB method[2] which did not correct for the impurity of the MTB. Thus, as regards accuracy or working range, the MRI procedure offers no discernible advantage over a simpler procedure evaluated earlier.

The diminished working range, at low sulfate levels, for the MRI procedure results, we believe, primarily from a sample-to-sample memory effect. This may be reduced as described previously.

VI. EVALUATION OF THE COLOVOS MODIFICATION OF THE MTB METHOD

A. Introduction

G. Colovos et al have described an empirical procedure for linearizing the MTB working curve in the range 0 to 100 μg/ml sulfate.[11] By decreasing sample dilution, this technique allows measurement in the range 0-10 μg/ml. For purpose of the present report the resulting procedure is referred to as the Colovos modification of the MTB method (Colovos-MTB).

Implicit in the Colovos procedure is the presumption that a 1:1 mole ratio of Ba:MTB provides the most linear working curve. The rationale for this presumption is given in Section V-A. Colovos et al determined the linearity of a series of working curves prepared with varying Ba-impure MTB ratios. If for example, a Ba-impure MTB mole ratio of 0.6[a] resulted in the most linear working curve, this ratio is presumed to provide a Ba:pure MTB mole ratio of 1:1 and is used for analyses. A spectrophotometric estimation of MTB purity can also be performed. However, this accounts for non-absorbing impurities only.

---

[a] Calculated using the molecular weight for pure MTB. This is therefore, only an approximation.

B. Linearizing the Working Curve

The Technicon system was set up as in the Midwest Research procedure described in Appendix E except that the rate used was 30 rather than 40 samples per hour. The spectrophotometric estimation for Eastman Kodak MTB, lot E3X, gave a 72.5% purity compared to the 78.5% obtained by the Midwest procedure. There was, however, insufficient MTB remaining from this lot for use with Colovos' empirical technique for determining MTB purity.

With Eastman Kodak Lot C5F, spectrophotometric analysis yielded a purity of 64.9%. This batch was used to prepare working curves ranging from 0.65 to 1.24 in Ba/impure MTB mole ratio. The degree of curvature for each working curve was evaluated by measuring the goodness of fit of a straight line regression for the 2-100 μg/ml data (Table 38). Based on the minimum in $S_{y.x}$ for a Ba/MTB mole ratio of 0.78, this ratio was selected for use in evaluating the Colovos procedure. This suggests a purity of ca. 78%.

Since this procedure was not performed on the same MTB lot as used with the Midwest procedure no direct comparison is possible. However, both lots were analyzed by spectrophotometry. Based on analyses of lot E3X (65%) a purity by the MRI method about 6% above that by spectrophotometry would be expected with lot C5F, or about 71%. This

Table 38

Straight Line Fitting as a Function of Concentration for the Colovos-MTB Method (% error)*

Sulfate Conc. (μg/ml)	Ba/MTB (mole ratio) 1.24	1.00	0.92	0.78	0.71	0.65
100	- 0.4	- 4.4	- 5.0	- 3.4	- 5.0	- 4.7
90	3.2	1.1	0.0	- 2.0	- 2.4	- 2.6
80	2.8	3.2	2.6	1.3	2.4	1.1
70	1.1	3.5	4.1	3.0	3.5	3.4
60	0.0	3.3	4.3	5.2	5.6	5.6
50	- 4.9	2.0	2.1	3.4	4.3	7.0
40	-10.4	- 1.0	- 0.8	1.6	3.6	4.2
30	-12.5	-18.0	- 1.0	1.6	4.5	4.5
20	-17.7	- 5.7	- 8.3	- 4.4	- 2.7	- 1.4
10	- 4.6	- 0.7	- 8.2	-11.4	-10.9	-10.1
7	13.7	7.8	-10.1	-14.3	-20.2	-17.9
5	35.5	15.3	- 4.1	-17.5	-21.4	-28.4
3	92.9	39.2	0.1	- 5.2	-21.1	-36.5
2	169.5	---	25.3	7.7	-40.2	-49.0

Regression Parameters

Intercept	-3.849	-2.211	0.185	-0.382	1.075	1.664
Slope	1.011	1.008	1.004	1.013	1.024	1.016
r	0.997	0.998	0.998	0.999	0.998	0.998
$S_{y.x}$	2.724	2.546	2.050	1.792	2.387	2.428

---

*: $\frac{\text{Obs.-True}}{\text{True}} \times 100\% = \%\ \text{error}$

is 7% below the observed purity by the Colovos procedure, a result which we consider equivalent within experimental uncertainty.

The working curves for Ba/MTB mole ratios 1.00, 0.78 and 0.71 are compared in Figure 21. A ratio 1.00 corresponds to a reagent prepared assuming the MTB to be 100% pure (note that Colovos and the Midwest methods differ in the specified Ba/100% MTB ratios; Colovos specified 1.00 while MRI specified 1.13). In all cases the curves remained distinctly S-shaped with an obvious increase in linearity for the mole ratios 0.71 and 0.78 ratios compared to 1.00.

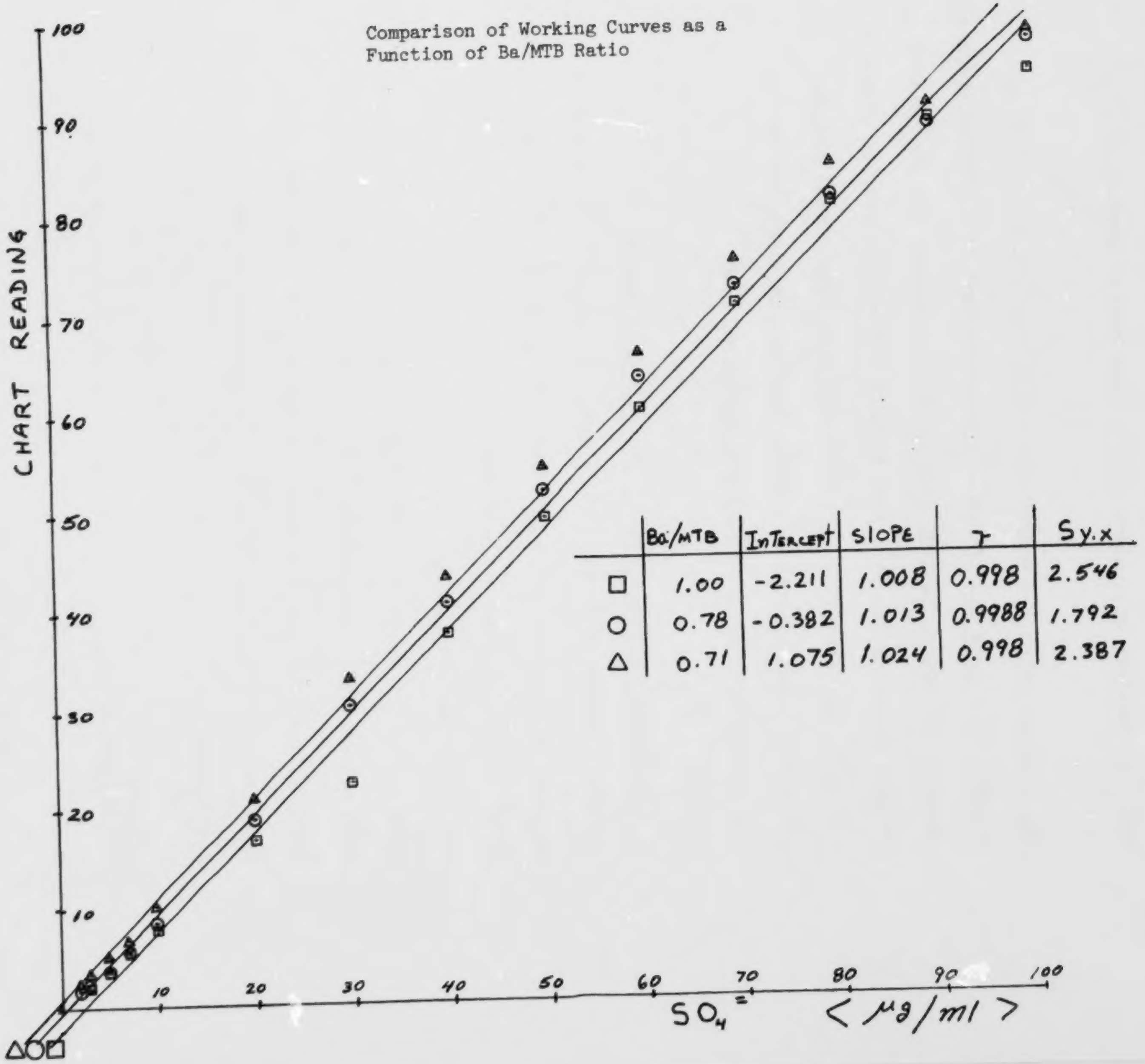
C. System Change for Operation in the 0-10 μg/ml Range

In normal operation of the MTB method, the sample is diluted 1 to 6. As noted by Colovos, the sensitivity can be increased by reducing the dilution. The system was modified to permit the analysis of the undiluted sample by using a 2 ml/min pump tubing for the sample, eliminating the water line, the sample air bubbler and the mixing coil but keeping the debubbler. The waste line pump tubing was changed to reduce the flow from 2 ml/min to 1.6. This was found necessary because the higher flow rate produced air bubbles in the colorimeter cell.

The reproducibility of the working curve from day to day using this system is shown for six trials in Table 39. The slope remained constant within about 5% but the intercept varied markedly. To illustrate the linearity of the working curve Figure 22 plots results for Trial 3; both the slope and the $S_{y.x}$ for this trial closely approximate the mean values for six trials.

Figure 21

Comparison of Working Curves as a
Function of Ba/MTB Ratio



	Ba/MTB	InTercept	SlOPE	r	Sy.x
□	1.00	-2.211	1.008	0.998	2.546
○	0.78	-0.382	1.013	0.9988	1.792
△	0.71	1.075	1.024	0.998	2.387

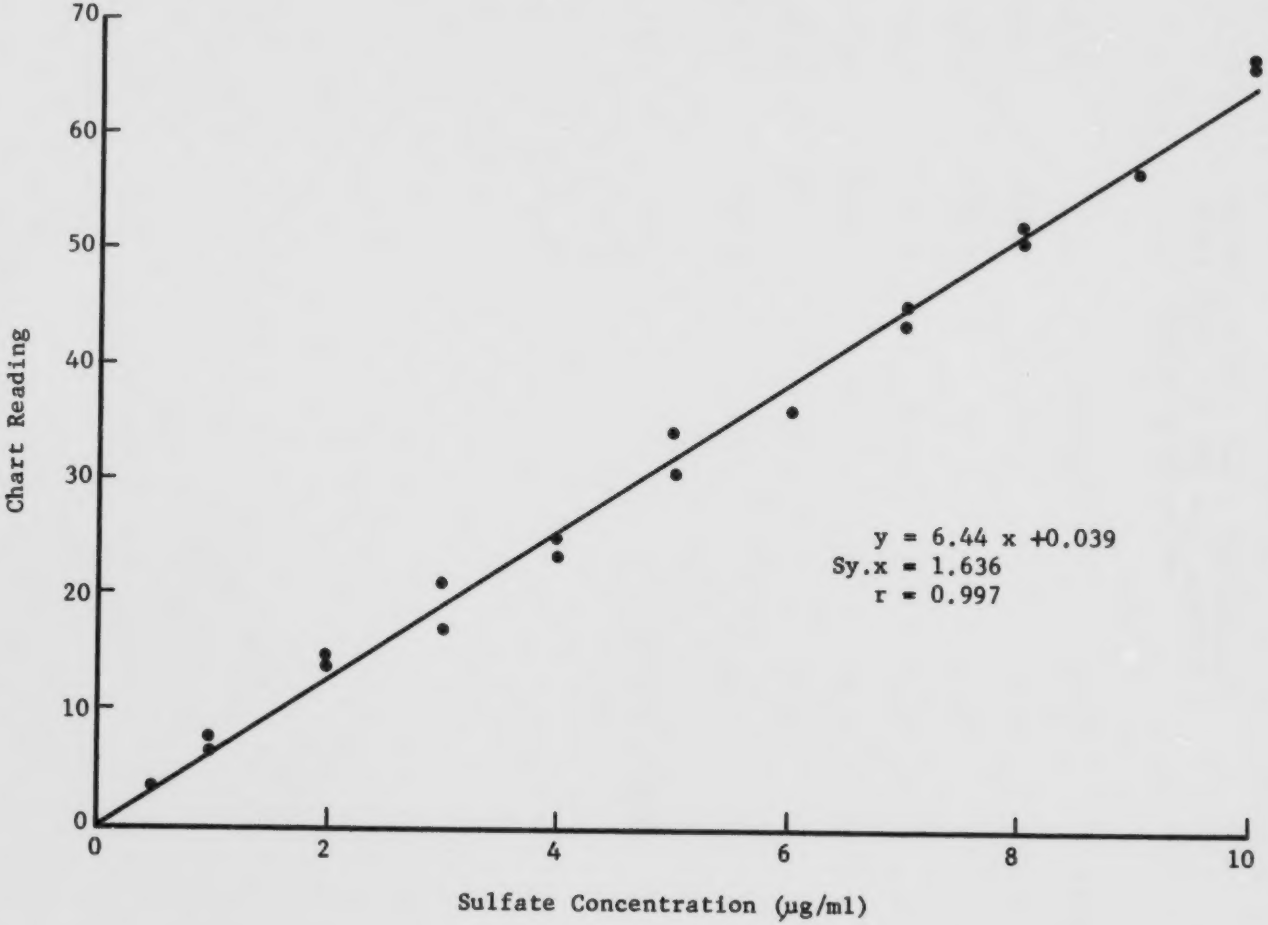
Table 39

Reproducibility and Linearity of the Working Curve for the Colovos-MTB Method (0-10 µg/ml)

Trial	Slope	Intercept	r	$S_{y.x}$
1	6.00	0.173	0.9967	1.460
2	6.13	-1.20	0.9870	3.062
3	6.44	0.039	0.9970	1.636
4	6.75	0.0638	0.9979	1.185
5	6.78	-1.68	0.9984	1.099
6	6.79	-1.14	0.9972	1.463
mean	6.48 ± .35			1.65

Figure 22

TYPICAL WORKING CURVE FOR COLOVOS-MTB METHOD
IN 0-10 μg/ml RANGE



D. Accuracy and Working Range

Glass fiber filter strips loaded with five levels of sulfate, four strips per level, were extracted following the MRI ultrasonic extraction procedure. Extracts were diluted to cover the range from 1 to 10 μg/ml. The results, therefore, are subject to error because of differences in accuracy and precision over this concentration range. As shown in Table 40, the results are 30% low at 1 μg/ml but are within 5% of the true value for concentrations of 4 to 9.8 μg/ml. Above 1 μg/ml the C.V. values remain $\leq$ 2%.

The concentrated atmospheric sample extract previously used for evaluating the turbidimetric and MRI-MTB methods was diluted to varying degrees to permit evaluation of relative accuracy and precision as a function of concentration and from these, the working range. The results are given in Table 41. The calculated, undiluted concentration of the extract showed no bias at 2 μg/ml and higher concentration. Thus the correct undiluted concentration was taken to be the mean of ten results, 143 ± 5 μg/ml. These compare to values from 139 to 148 found by five other procedures as given in footnote b to Table 41.

The ratios of observed to expected concentrations are plotted against expected concentration in Figure 23. The results indicate accuracy within 5% of the optimal value in the concentration range from 2 to 10 μg/ml. The coefficient of variation of three trials are plotted against concentration in Figure 24. The C.V. values remain < 5% (with one outlier) in the range 2-10 μg/ml. We conclude that, based on relative accuracy and precision as measured by C.V., the working

Table 40

Analysis of Sulfate EPA Audit Strips by the Colovos-MTB Method

Sample	Approximate Concentration Analyzed (µg/ml)	Theoretical Value (µg/strip)	Observed Value (µg/strip)	C.V. (%)	$\frac{\text{Observed}}{\text{Theoretical}}$
9000 Series	1	745.6	514 ± 43	8.4	0.69
5000 Series	2.7	2670.1	2360 ± 4	0.2	0.88
1000 Series	4	200.2	193 ± 3	1.6	0.96
8000 Series	7	1737.2	1770 ± 38	2.2	1.02
7000 Series	9.8	4240.2	4456 ± 57	1.3	1.05

Regression Equation: $y = 0.17 + 6.00X$

$r = 0.9967$

$S_{y.x} = 1.460$

Table 41

Relative Accuracy and Precision of Colovos-MTB Method with an Atmospheric Sample (μg $SO_4^{=}$/ml)[a]

Concentration % of Undiluted	Observed Mean of 3 Trials	σ	C.V. (%)	Calculated Undiluted Concentration	Expected Diluted Concentration	Observed Conc. / Expected Conc.
0.36	0.83	0.46	55.85	231	0.52	1.59
0.72	0.82	0.14	16.58	114	1.03	0.79
1.44	2.07	0.08	3.95	144	2.06	1.00
1.80	2.53	0.05	1.81	141	2.58	0.98
2.16	2.88	0.07	2.56	133	3.09	0.93
2.88	3.97	0.04	1.02	138	4.12	0.96
3.60	5.35	0.39	7.25	149	5.16	1.03
4.32	6.17	0.25	4.12	143	6.19	0.99
5.04	7.22	0.35	4.78	143	7.22	1.00
5.76	8.18	0.29	3.55	142	8.25	0.99
6.47	9.75	0.34	3.51	151	9.27	1.05
7.19	10.65	0.44	4.08	148	10.30	1.03

Mean undiluted = 143.2 ± 5.3

a. Data reduction by linear regression.

b. Compares to results (μg/ml):
  AIHL Method 61 : 141.8 ± 4.8
  Optimized turbidimetric: 139.4 ± 4.7
  SulfaVer : 143.5 ± 4.7
  Midwest MTB (3rd order): 137 ± 3.6
  Dionex IC : 148.2 ± 1

Figure 23
RELATIVE ACCURACY AS A FUNCTION OF SULFATE CONCENTRATION
WITH THE COLOVOS-MTB METHOD

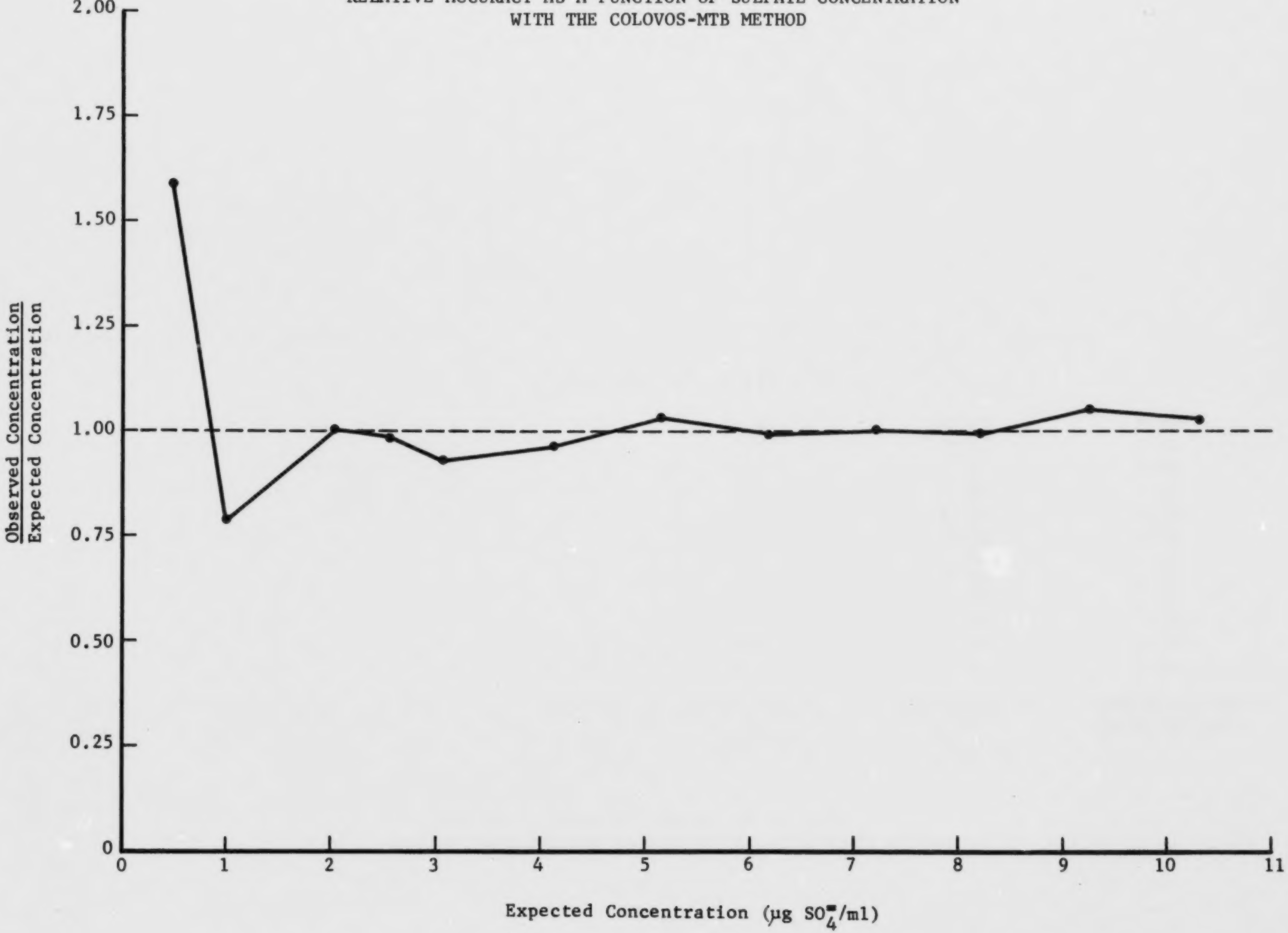
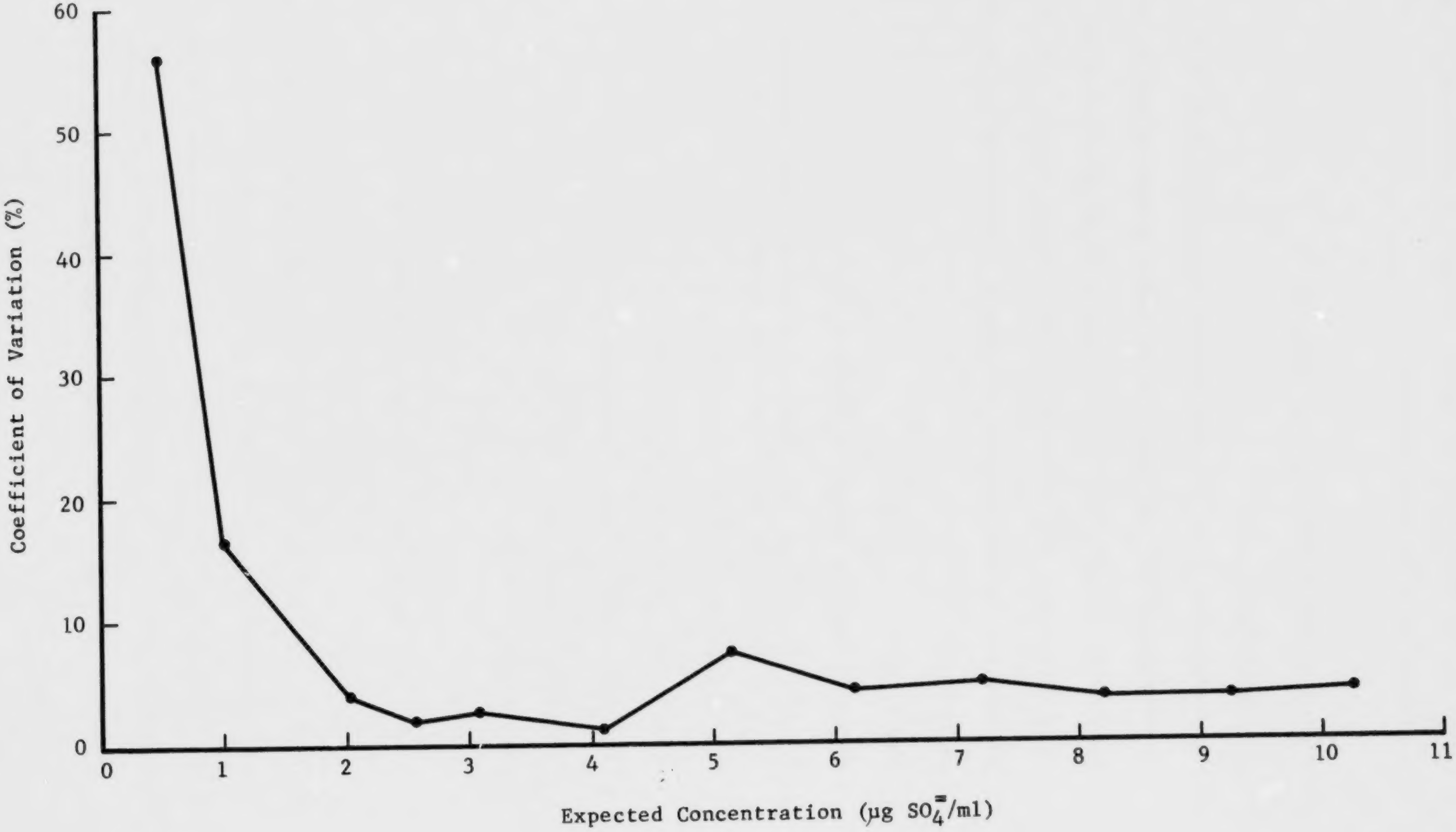


Figure 24

COEFFICIENT OF VARIATION AS A FUNCTION OF SULFATE CONCENTRATION
WITH THE COLOVOS-MTB METHOD



range of the Colovos modification of the MTB method, (0-10 μg/ml) is from 2 to ≥ 10 μg/ml sulfate.

VII. EVALUATION OF THE DIONEX ION CHROMATOGRAPH

A. Introduction

On recommendation of the EPA Project Officer a Dionex Model 10 ion chromatograph (IC) was modified by water jacketing and thermostatting the column and detector and insulating these as well as the Teflon solution lines. The unit was operated with a Varian A-25 recorder and Spectra-Physics Autolab Minigrator. Operating parameters were as follows:

Temp: 35°C

Eluent: 0.0030 M $NaHCO_3$ + 0.0024 M Na_2CO_3

Column: 3 x 100 mm precolumn + 3 x 500 mm anion separator
6 x 250 mm anion supressor column

Eluent flow rate: 2.5 - 3.3 ml/minute

Ranges: 10, 3, and 1 μmho

Recorder: 1 volt input (full scale)

Minigrator: peak width = 99 seconds

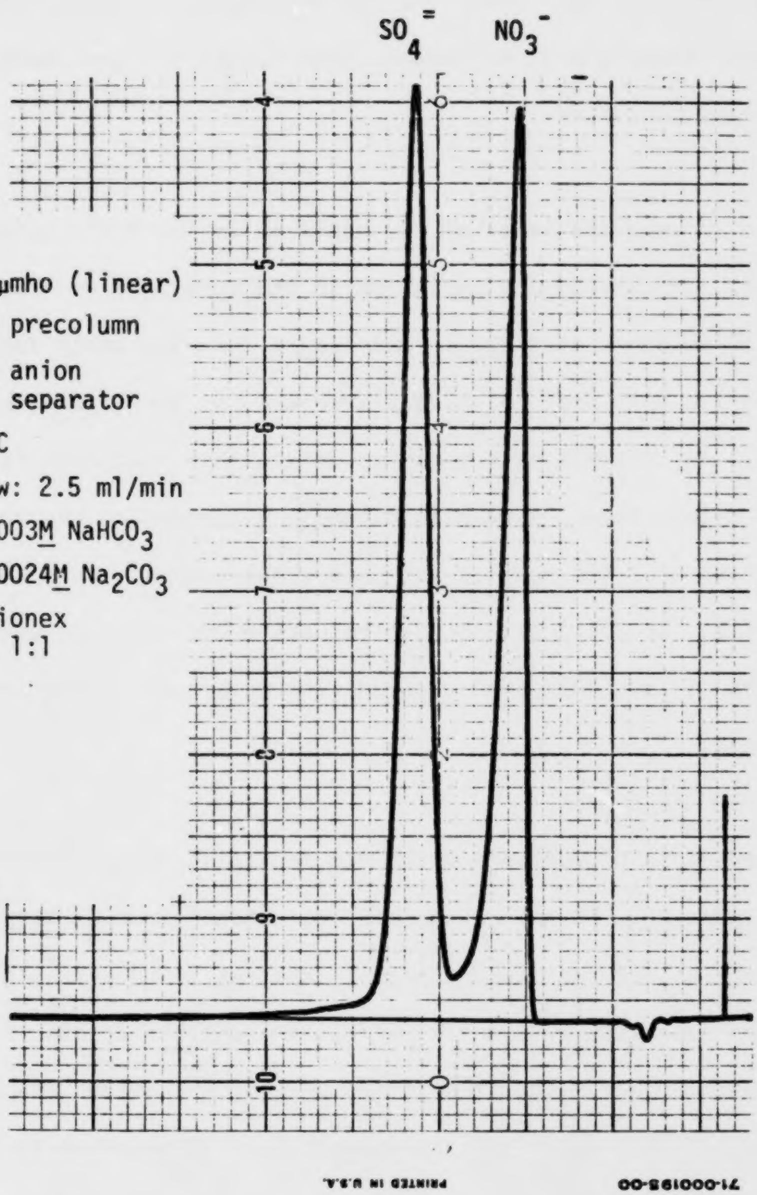
Sample loop: 30 μl

A detailed protocol is included as Appendix F.

In addition to peak area, peak height was determined manually by subtracting the middle of the baseline trace from the middle of the peak trace. The nitrate and sulfate peaks were not completely resolved when present at similar concentrations (Figure 25). The effect of this small overlap on sulfate determination is reported in Section VIII.

Figure 25

Resolution of Sulfate and Nitrate at Equal Concentrations by Ion Chromatography



Range: 10 µmho (linear)

3 x 100 mm precolumn

3 x 500 mm anion separator

Temp: 35°C

Eluent Flow: 2.5 ml/min

Eluent: 0.003M $NaHCO_3$
0.0024M Na_2CO_3

Recorder/Dionex Response 1:1

B. Reproducibility of Working Curves and Linearity of Range Switch

Initial objectives in evaluating the IC were 1) to establish the reproducibility of the working curve set on a range suitable to provide analysis in the 0-150 μg/ml range, 2) to determine if calibrations obtained on a given range were directly applicable to other ranges after correction for the change in μmhos corresponding to full scale and 3) to compare peak height and peak area techniques for data reduction.

Range 10 μmho was selected for analysis in the 0-150 μg/ml sulfate range. The day-to-day variation in the working curve for three trials is shown in Table 42 and Figure 26. The table includes results employing both peak height and area and for the figure, peak heights only. An analysis of covariance established that results by the peak height method were significantly different on the three days. Inspection of the results for peak areas suggests this is true here as well. Accordingly, the determination of a working curve must be a part of any analytical protocol for daily use of the ion chromatograph.

A comparison of working curves for ranges 1, 3, and 10 μmho is shown in Figure 27. No effort was made to attenuate or amplify the output voltage at the recorder. Range 1 μmho was found suitable for working curves extending to about 30 μg/ml, whereas the 3 μmho, range was good for working curves up to about 80 μg/ml. The curve obtained for 10 μmho includes all results for the three trials illustrated in Figure 26. No allowance could be made for day-to-day variability in the data for ranges 1 and 3 μmho.

Table 42

Reproducibility of Working Curve for Dionex Ion Chromatograph (Range: 10 μmho)

Trial	a		b		r		$S_{y.x}$	
	pk. ht.	pk. area	pk. ht.	pk. area	pk. ht.	pk. area	pk. ht.	pk. area
1	-0.38	-0.90×10^5	0.332	1.59×10^5	0.9997	0.9996	0.361	2.18×10^5
2	-0.09	-1.12×10^5	0.293	1.52×10^5	0.9997	0.9999	0.346	1.20×10^5
3	-0.28	-2.81×10^5	0.346	1.68×10^5	0.9997	0.9997	0.407	2.03×10^5

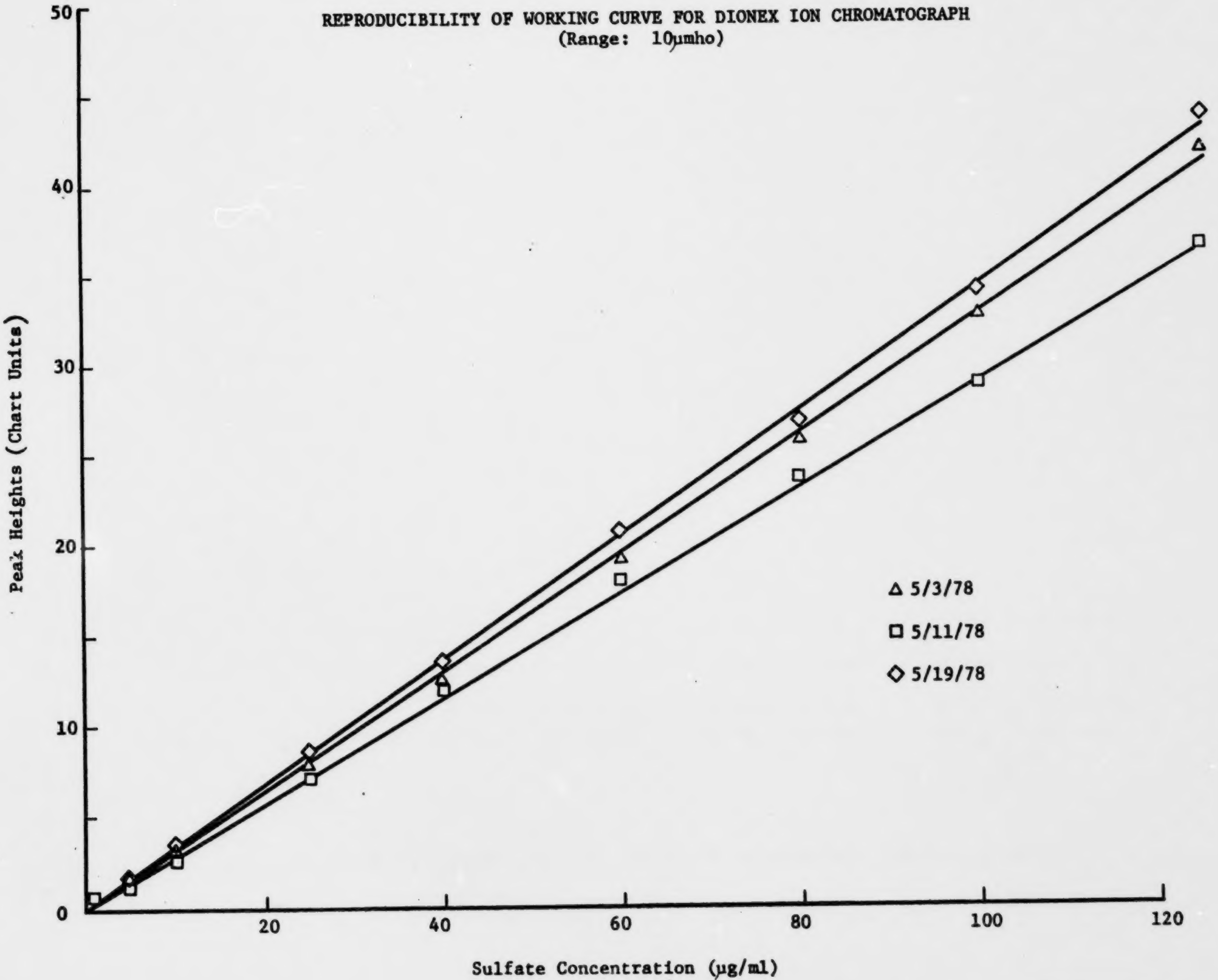
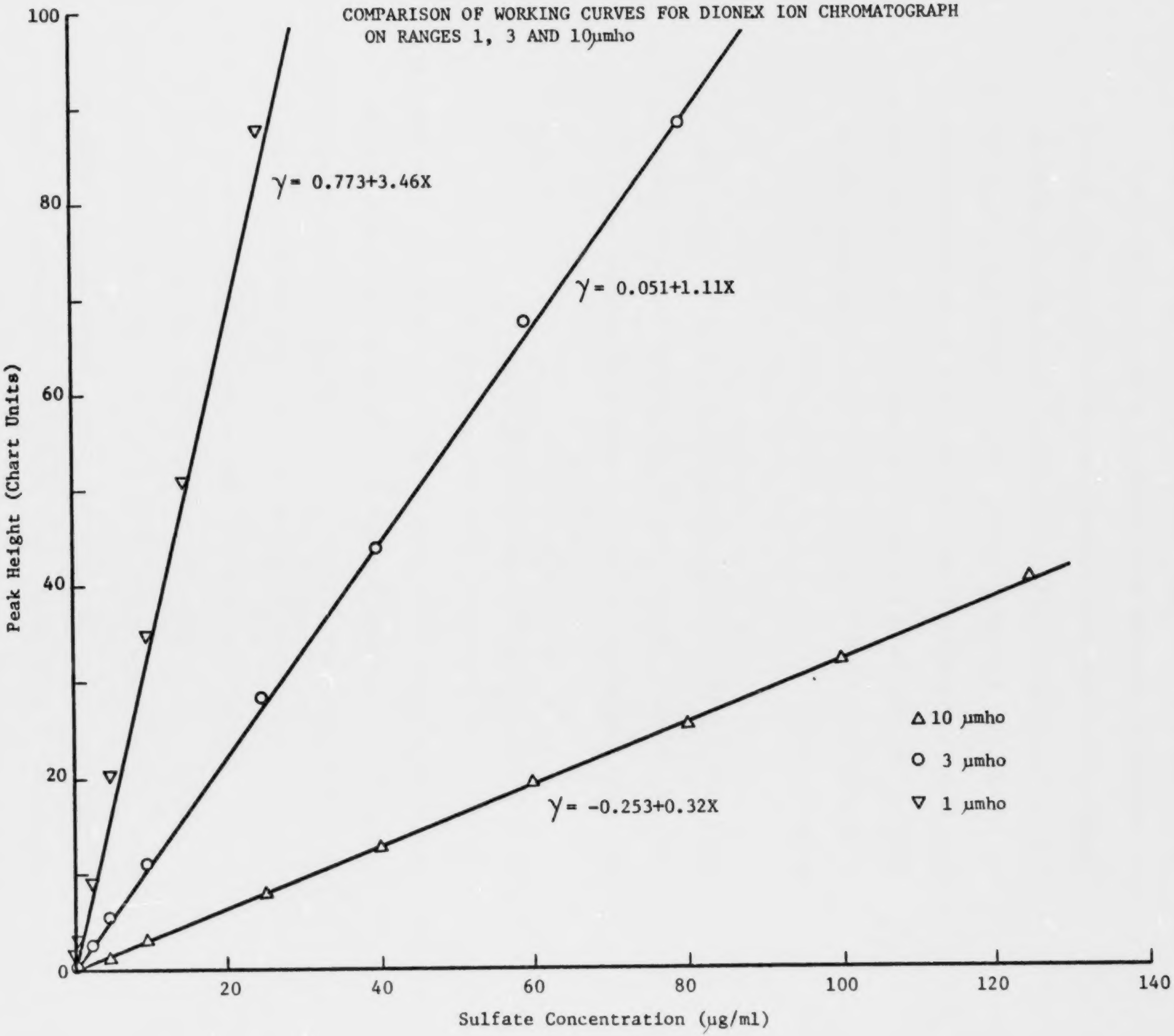

REPRODUCIBILITY OF WORKING CURVE FOR DIONEX ION CHROMATOGRAPH
(Range: 10μmho)

Figure 26



COMPARISON OF WORKING CURVES FOR DIONEX ION CHROMATOGRAPH ON RANGES 1, 3 AND 10μmho

Figure 27

Since the difference in intercepts for the three curves is small, the linearity of the range switches can be evaluated by plotting the regression equation slopes against 1/μmho for full scale (Figure 28). These data suggest that calibration curves run on a given range can be used to determine, approximately, samples run on the same day using another range. For example, using the regression equation from range 10 μmho, with slope multiplied by 10/3 and the peak height observed on range 3 for a 25 μg/ml sample, a concentration of 26.7 μg/ml is calculated. This represents an error of +7%.

Based on these initial results there appeared to be relatively little distinction between use of peak heights and peak areas. An additional comparison of these procedures is included below.

C. Accuracy with EPA Sulfate Audit Filter Strips

Extracts of 20 EPA sulfate audit strips (four at each of five levels), were analyzed by IC using range 10 μmho only (Table 43). The analyses were performed on three separate days for which individual working curves were prepared with three or four standards. The concentration of the extracts ranged from 4 to 85 μg/ml. The results indicate a positive bias in all cases with less accuracy and precision at $\leq$ 15 μg/ml. At higher concentrations the results were accurate within 7% using peak heights with a C.V. of $\leq$ 9%. The persistent positive bias may reflect, in part, the effect of slight overlap of nitrate and sulfate peaks. This would be particularly significant for the 9000 series samples which, had a relatively large proportion of nitrate. ($SO_4^{=}/NO_3^{-}$ = 0.6 w/w). The peak height

REGRESSION EQUATION SLOPE AGAINST 1⁄µmho
FOR FULL SCALE WITH DIONEX ION CHROMATOGRAPH

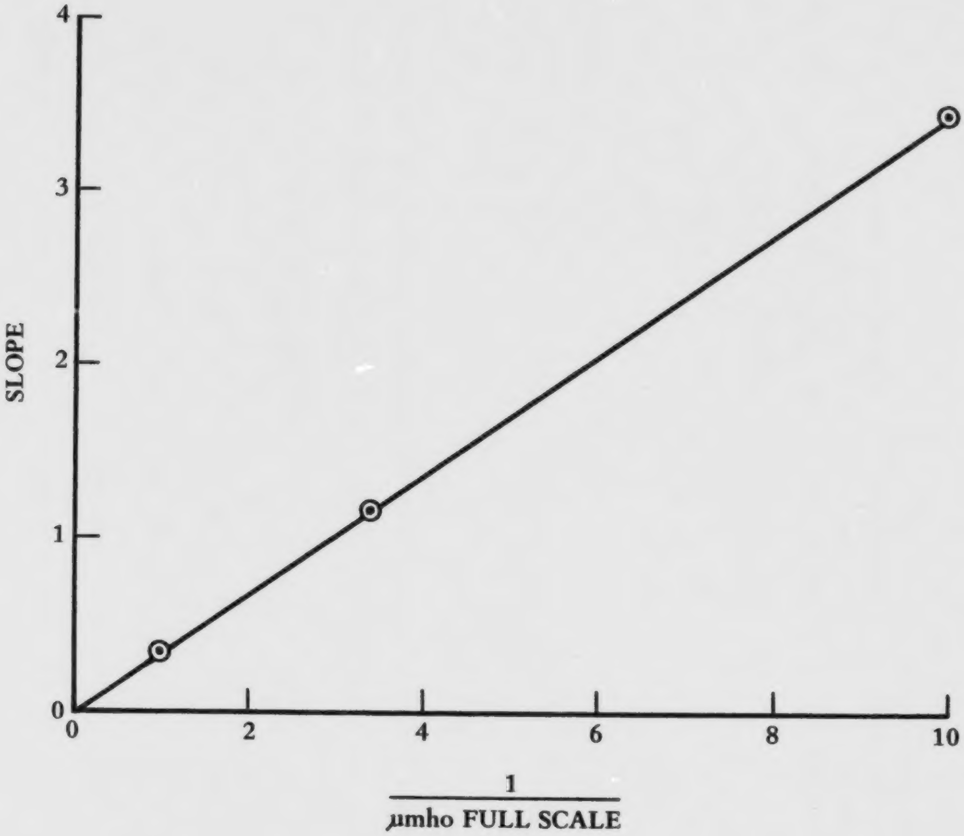


Figure 28

Table 43

ANALYSIS OF EPA SULFATE AUDIT STRIPS BY THE DIONEX ION CHROMATOGRAPH[a]

Sample	Approximate Concentration Analyzed (μg/ml)	Theoretical Value (μg/strip)	Observed Value (μg/strip)		C.V.(%)		Observed / Theoretical	
			Pk. Ht.	Pk. Area	Pk. Ht.	Pk. Area	Pk. Ht.	Pk. Area
1000 Series	4	200.2	282	436	19.6	166	1.41	2.18
9000 Series[b]	15	745.6	865	999	11.1	37.7	1.16	1.34
8000 Series	35	1737.2	1862	1929	9.0	15.5	1.07	1.11
5000 Series	53	2670.1	2787	2681	3.7	3.0	1.04	1.00
7000 Series	85	4240.2	4425	4224	0.8	7.9	1.04	1.00

---

a. Results are mean values ± 1 σ for four strips from each series extracted by 30 minutes ultrasonic extraction.

b. The weight ratio sulfate/nitrate in this series was 0.6 compared to 2.2 to 12 for the other series.

Regression Equations
(peak height)

Day	a	b	r	$S_{y.x}$
1	-0.233	0.441	0.9999	0.122
2	-0.709	0.465	0.9995	0.600
3	-0.527	0.434	0.9999	0.275

technique yielded results with generally better accuracy and precision compared to the peak area technique.

D. Working Range

The concentrated atmospheric sample extract previously used for evaluating the turbidimetric and MTB methods was diluted to varying degrees to permit evaluation of relative accuracy and precision as a function of concentration. The results are given in Table 44. The calculated undiluted concentration was taken as the mean of five results between 12.5 and 43.75% dilution, 148 ± 1 μg/ml. This compares to 139 ± 4.7, 139 ± 4.5, 142 ± 4.9 and 144 ± 4.7 μg/ml by Method 75, MRI-MTB, Method 61 and SulfaVer^R IV procedures, respectively. The peak height ratio nitrate/sulfate for this series of samples was 2.0 ± .2. Thus some positive interference from nitrate might be expected. The ratio of observed to expected concentrations are plotted against expected concentration in Figure 29. The results indicate relative accuracy within 5% in the range 7 to 111 μg/ml. The coefficients of variation of three independent trials are plotted against expected concentration in Figure 30. The C.V. values generally decreased with increasing sulfate concentration but remained below 5% at ≥ 7 μg/ml.

Based on both relative accuracy and precision, as measured by coefficients of variation, the working range of the Dionex ion chromatograph on range 10 μmho is from about 7 to ca. 111 μg/ml.

Table 44

Relative Accuracy and Precision of the Dionex Ion Chromatograph, Range 10 μmho
(μg $SO_4^{=}$/ml)

Concentration, % of Undiluted	Observed Mean of 3 Trials	σ	C.V. %	Calculated Undiluted Conc.	Expected Diluted Conc.	$\frac{\text{Observed Conc.}}{\text{Expected Conc.}}$
2.5	4.12	0.37	8.88	164.67	3.70	1.112
5.0	7.43	0.27	3.61	148.67	7.41	1.003
7.5	10.99	0.30	2.72	146.53	11.11	0.989
10.0	14.31	0.65	4.54	143.13	14.82	0.966
12.5	18.49	0.47	2.52	147.89	18.52	0.998
15.0	22.19	0.67	3.02	147.96	22.23	0.998
18.75	27.58	0.25	0.91	147.08	27.79	0.993
31.25	46.78	0.94	2.01	149.71	46.31	1.010
43.75	64.88	1.74	2.68	148.30	64.83	1.001
56.25	85.36	0.30	0.35	151.75	83.36	1.024
75.0	115.63	0.28	0.24	154.18	111.14	1.040
87.5	142.25	0.80	0.56	162.57	129.66	1.097
100	167.13	1.30	0.78	167.13	148.19	1.128

Mean Undiluted = 148.2 ± 1

Coefficients for Linear Regression Working Curves

Trial	Intercept	Slope	r	$S_{y.x}$
I	-0.3037	0.4064	0.9993	1.074
II	-0.0581	0.4192	0.9999	0.390
III	-0.1358	0.4397	0.9999	0.289

Figure 29

RELATIVE ACCURACY AS A FUNCTION OF SULFATE CONCENTRATION
WITH THE DIONEX ION CHROMATOGRAPH (Range 10µmho)

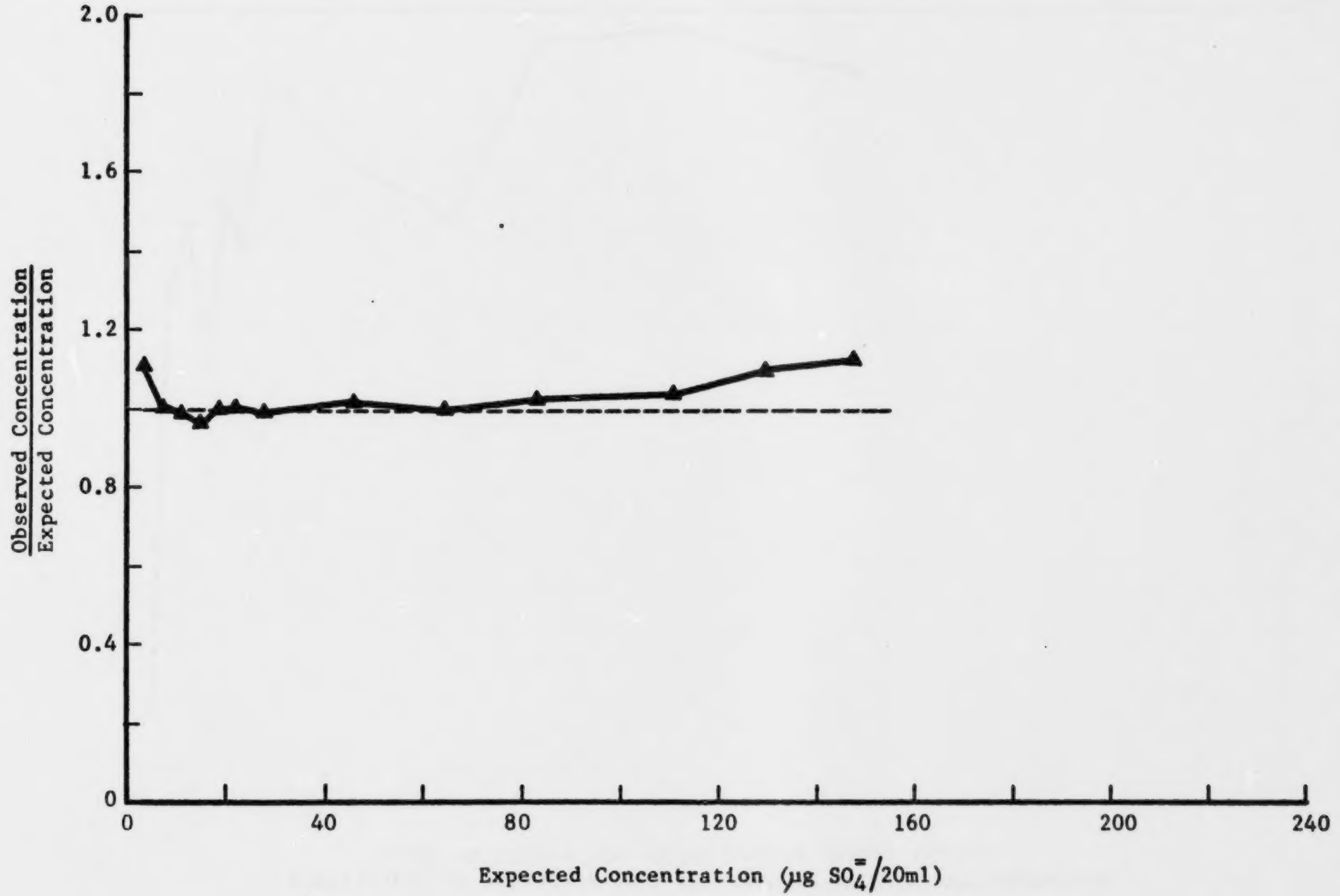
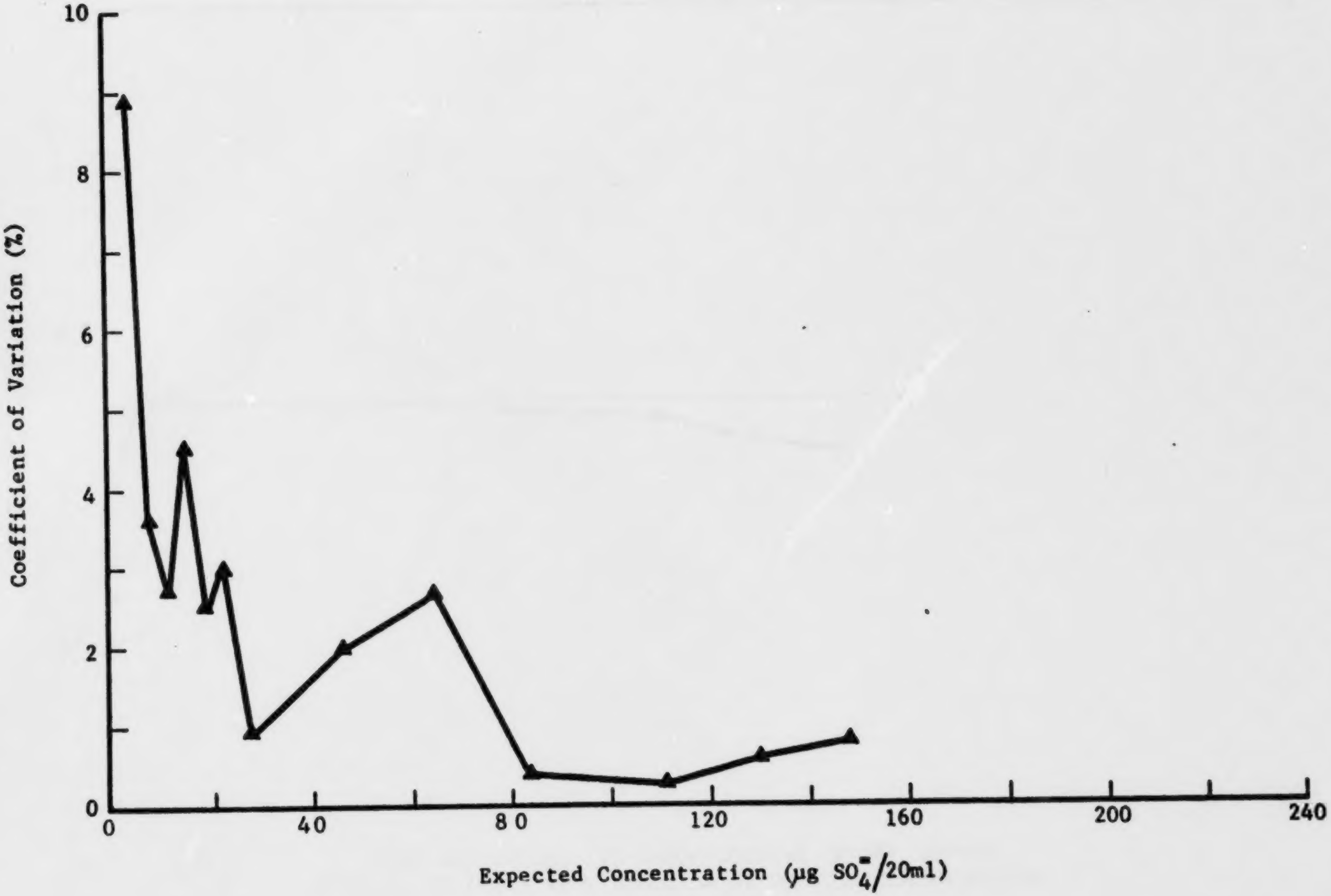


Figure 30

COEFFICIENT OF VARIATION AS A FUNCTION OF SULFATE CONCENTRATION
WITH THE DIONEX ION CHROMATOGRAPH (Range 10μmho)



VIII. INTERFERENCE EFFECTS

A. Introduction

Previous AIHL studies have included effects of potential interferents singly, in pairs and quartets in relation to a series of sulfate methods.[1,2] Interferents selected for study and their concentrations were based, in part, on measurements of atmospheric particulates. The present study includes four potential interferents: phosphate, colloidal clay (to simulate turbid extracts), water-soluble organics contributing absorbance in 400-500 nm range as isolated from California atmospheric samples, and bicarbonate. The isolation of the organics is described in Appendix G.

The scheme for the study is shown in Table 45. Phosphate was studied only with MTB procedures based on previous work indicating significant interference and high phosphate levels (ca. 2000 μg/8 x 10" filter) in early batches of Gelman "EPA Grade" filters.[2] As with clay, concentrations were decreased tenfold for the Colovos MTB. The levels of colloidal clay used were chosen based on prior evaluation of the turbidity of atmospheric extracts prepared from 3/4 x 8" strips from 24-hour hi-vol filter samples collected in St. Louis.[2] The maximum turbidity observed was equivalent to that of a colloidal suspension of 40 μg/ml bentonite clay or 25 μg/ml kaolinite. For analysis based on use of 1/4 of a 8 x 10" filter the maximum turbidity expected was calculated as 65 μg/ml kaolinite. This calculation was used to set concentrations for the Midwest MTB and Method 75. Because of smaller samples anticipated with use of the Colovos method in the 0-10 μg/ml sulfate range, concentrations of clay were decreased by a factor of 10.

Table 45

Sulfate and Interferent Levels for Interference Studies

Method	$(SO_4^{=})$ μg/ml	$(PO_4^{\equiv})$ μg/ml	Colloidal clay[a] (μg/ml)	Organics from Atmos. Ext.[b] Abs./cm at 400 nm	(HCO_3^{-}) μg/ml
MRI MTB	10	10, 5, 2.5, 1.25	75, 50, 25, 10	.1, .05, .025, .0125	--
(0-100 μg/ml $SO_4^{=}$)	35	10, 5, 2.5, 1.25	75, 50, 25, 10	.1, .05, .025, .0125	--
	60	10, 5, 2.5, 1.25	75, 50, 25, 10	.1, .05, .025, .0125	--
Colovos MTB	1.5	1.0, 0.5, 0.25, 0.125	7.5, 5, 2.5, 1.0	.05, .025, .0125, .006	--
(0-10 μg/ml $SO_4^{=}$)	5	1.0, 0.5, 0.25, 0.125	7.5, 5, 2.5, 1.0	.05, .025, .0125, .006	--
	8.5	1.0, 0.5, 0.25, 0.125	7.5, 5, 2.5, 1.0	.05, .025, .0125, .006	--
Method 75	10	--	75, 50, 25, 10	.1, .05, .025, .0125	30,15,7.5,3.8
	35	--	75, 50, 25, 10	.1, .05, .025, .0125	30,15,7.5,3.8
	60	--	75, 50, 25, 10	.1, .05, .025, .0125	30,15,7.5,3.8

a. Using kaolinite clay

b. Extracted by the procedure given in Appendix G.

Similarly, based on the previous study[2] the maximum level of organics expected, as measured by absorbance at 400 nm for extraction of one quarter filter is A = 0.07. The bicarbonate concentrations selected were based on preliminary results[1] which showed a slight positive interference with 10 μg/ml bicarbonate for one version of the $BaSO_4$ turbidimetric method.

B. Method 75

The results of the interference study with Method 75 using third order regression are shown in Table 46. While analyses are performed on 20 ml samples, results have been expressed per ml of solution for ease in comparison with other methods. Colloidal clay showed the largest interference. Its interference was clearly observable at all sulfate levels but was largest at low sulfate. Increasing concentrations of clay produced a decreasing observed sulfate value. However, at low levels of sulfate and high clay concentrations results became erratic.

Organics produced a measurable (up to 17%) negative interference at the lowest sulfate level. At higher sulfate values no interference was observable. Bicarbonate did not interfere at any sulfate level.

C. Midwest Research Institute-MTB Method

Results with the MRI-MTB method are shown in Table 47. At 10 μg/ml sulfate, results are shown without added interferent because, using linear regression, the method yields low values at this level. At 10 μg/ml sulfate no interferences are observable in part because of

Table 46

Interference Effect with the AIHL Method 75 (μg/ml Observed Sulfate)[a]

Sulfate Level μg/ml	10				35				60			
Interferent Level[b]	A	B	C	D	A	B	C	D	A	B	C	D
Interferent												
Colloidal clay	8.8 1.6	5.2 2.3	1.6[c] ---	2.9[d] 1.0	35.3 0.5	33.2 0.3	31.2 0.2	30.0 0.6	58.3 0.9	56.2 1.2	53.0 0.7	50.7 0.7
Organics	9.4 0.9	9.9 0.3	9.4 0.3	8.3 0.3	35.4 1.9	35.8 0.5	35.2 0.7	35.2 0.4	60.0 0.7	60.5 0.5	59.0 1.1	59.1 2.4
bicarbonate (HCO_3^-)	10.2 0.2	10.1 0.7	10.0 0.6	10.4 0.3	37.0 0.3	36.1 0.2	36.5 0.5	36.0 0.6	60.0 0.3	59.5 0.9	60.2 0.8	60.0 0.6

a. Mean of three determinations, third order regression, with ± 1 σ values shown below mean.

b. Interferent concentrations:

	A	B	C	D
Colloidal clay (μg/ml)	10	25	50	75
Organics (Abs/cm at 400 nm)	0.0125	0.025	0.05	0.1
bicarbonate (μg/ml)	3.8	7.5	15	30

c. Single value. Two trials yielded negative results.

d. Mean of two results. One value yielded negative results.

Table 47

Interference Effects with the MRI-MTB Method[a]

Sulfate Level µg/ml	10					35				60			
Interferent Level[b]	0[c]	A	B	C	D	A	B	C	D	A	B	C	D
Interferent:													
Colloidal clay	8.0 2.7	10.1 1.7	7.8 0.7	7.6 0.7	7.7 0.6	35.6 0.7	35.7 0.6	33.1 4.2	36.7 0.7	60.7 1.3	62.2 0.4	62.7 1.0	63.2 0.5
Organics	8.0 2.7	9.7 0.8	7.3 1.0	7.3 0.7	7.3 0.7	33.5 0.6	35.4 0.5	35.9 0.4	36.2 0.3	61.2 1.2	61.9 0.5	62.5 1.3	63.8 1.1
Phosphate	7.7 1.7	6.5 0.5	6.7 0.8	7.7 0.4	9.2 1.5	36.0 0.3	35.7 0.4	36.4 0.4	36.1 0.4	61.8 1.3	63.0 0.5	62.8 0.9	63.1 1.9

a. Mean of three determinations, third order regression, with ± 1 σ values shown below mean.

b. Interferent concentrations:

	A	B	C	D
Colloidal clay (µg/ml)	10	25	50	75
Organics (abs/cm at 400 nm)	0.0125	0.025	0.05	0.1
Phosphate (µg/ml)	1.25	2.5	5	10

c. Deviations from true sulfate level reflect poor fit of linear regression equation at this level the relatively poor precision of the method observed at this concentration. At 35 and 60 μg/ml sulfate, colloidal clay and organics exhibit small positive interference. Interference from phosphate at ≤ 10 μg/ml was not clearly established at any of the three sulfate levels.

D. Colovos MTB Method (0-10 μg/ml range)

Results with the Colovos MTB method are given in Table 48. At 1.5 μg/ml sulfate only organics exhibit a measurable interference. The positive interference by yellow organics is more easily seen at 5 and 8.5 μg/ml sulfate. Colloidal clay shows evidence of positive interference at 5 and 8.5 μg/ml sulfate. No clear evidence of phosphate interference is seen. As expected, these results are similar to those observed with the MRI-MTB method in the 0-100 μg/ml.

E. Dionex Ion Chromatograph

1. Introduction

Results obtained using EPA audit strips containing both sulfate and nitrate, the evaluation of relative accuracy, and the inter-method comparison results in Section IX suggest that the ion chromatograph sulfate results may be up to 5% high. A potential source of some of this error is the slight overlap of the nitrate and sulfate peaks observed during the current program. In principle, the mutual influence of such ions could be eliminated by employing standards prepared with both sulfate and nitrate at about the same levels as in the samples. However, because of the variability in the sulfate to nitrate ratio in atmospheric samples, this approach appears impractical.

Table 48

Interference Effect with the Colovos MTB Method (μg/ml Observed Sulfate)[a]

Sulfate Level μg/ml	1.5[c]				5.0				8.5			
Interferent Level	A	B	C	D	A	B	C	D	A	B	C	D
Interferent												
Colloidal clay	1.67	1.46	1.47	1.46	5.00	5.05	5.11	5.19	8.69	8.91	9.17	9.05
	0.16	0.02	0.00	0.02	0.23	0.12	0.06	0.05	0.24	0.15	0.07	0.08
Organics	1.57	1.46	1.57	1.83	5.10	5.17	5.26	5.59	8.72	8.97	9.22	9.44
	0.18	0.06	0.03	0.04	0.15	0.13	0.03	0.03	0.35	0.09	0.03	0.04
Phosphate ($PO_4^{\equiv}$)	1.31	1.68	1.23	1.23	5.03	4.98	5.70	5.05	9.51	8.91	8.84	9.03
	0.06	0.41	0.01	0.01	0.02	0.11	0.60	0.04	0.94	0.05	0.07	0.09

a. Except as noted, mean of three determinations, linear regression with ± 1 σ values shown below mean.

b. Interferent concentrations:

	A	B	C	D
Colloidal clay (μg/ml)	1.0	2.0	5.0	7.5
Organics (Abs/cm at 400 nm)	0.006	0.0125	0.025	0.05
Phosphate (μg/ml)	0.125	0.25	0.50	1.0

c. Mean of two results. One set of results yielded values which were too high because of a poor fit of the working curve at 1 μg/ml using linear regression.

The current study employed a 3 x 500 mm anion separator column which was close to the end of its useful life. Accordingly, the extent of nitrate interference with this column was evaluated together with that for a new column. While no evaluation of the interference of sulfate in nitrate determination was made, similar results would be expected.

2. Results

Standards containing from 20 to 80 μg/ml sulfate and 4 to 80 μg/ml nitrate were analyzed and compared to results for sulfate standards of equal concentrations without nitrate. The latter were run in succession with the mixed standard of equal sulfate level. The interference was judged by a change in the peak height for sulfate compared to that for the sulfate standard. Since peak heights are used for constructing working curves (which have negligible intercepts) the percentage change in peak heights equals the percentage change in observed concentration.

Results are given in Table 49 for both the old and new anion separator column. Flow rates were varied from 2.5 to 3.3 ml/min and the temperature from 23 to 35°C. Retention times for sulfate and nitrate were markedly lower for the old column. However, the retention time difference between sulfate and nitrate had decreased by only 19 seconds (11%). At 20 μg/ml, sulfate and nitrate interference was not reliably measured. Results at 40 and 80 μg/ml sulfate with equal concentration (by weight) of nitrate, showed increased sulfate signal with both the old and new columns. For

Table 49

Interference of Nitrate in Sulfate Determination with the Dionex Ion Chromatograph

Eluent Flow Rate (ml/min)	Column Temp. (°C)	Column	True Conc. (μg/ml)		Nitrate Interference (%)
			$SO_4^=$	NO_3^-	
3.26	35	Old	20	20	0.0
3.26	35	New	20	20	0.0
2.50	23	New	20	20	+5.7
3.26	35	Old	40	4	+1.1
3.26	35	Old	40	40	+3.6
3.26	35	Old	40	40	+3.2
3.26	35	Old	40	40	+2.5
3.26	35	New	40	40	+0.7
2.50	23	New	40	40	+1.8
3.26	35	Old	80	80	+3.2
3.26	35	Old	80	80	+4.0
3.26	35	New	80	80	+3.0
2.50	35	New	80	80	+4.3
2.50	35	New	80	80	+1.7
2.50	23	New	80	80	+1.8

Retention Times (seconds):	$SO_4^=$	NO_3^-	Δt
Old column	380	220	160
New column	657	478	179

the old column the increase averaged 3.3 ± .6% and for the new column, 2.2 ± 1.3%. We conclude, therefore, that a small positive bias in sulfate results is unavoidable using the ion chromatograph with the eluent, flow rates and temperatures studied. These findings provide at least partial explanation for the high results noted in evaluating the ion chromatograph for sulfate determination.

IX. INTERMETHOD COMPARISON WITH ATMOSPHERIC SAMPLES

A. Introduction

Twenty-four hi-vol filter samples collected on Gelman EPA Grade filters were selected for use in comparing analytical results among the sulfate methods evaluated in the current study. These include Method 75, Colovos MTB, MRI-MTB, SulfaVer^R and the Dionex ion chromatographic methods. In addition, the samples were analyzed by the AIHL microchemical method with ion exchange pretreatment.[7,9]

The samples analyzed were obtained from the California Air Resources Board, They were selected from a set of 50, with five collected at each of 10 sites throughout California. Samples were visually graded into categories "light", "medium" and "heavy" loadings. Where possible, samples from at least two of these loading categories at each site were used for this study (Table 50). The samples included an equal number collected within and outside of the South Coast Air Basin.

One-half of each 8 x 10" filter was extracted by 30 minute ultrasonic extraction with final volume 200 ml. The filtered, aqueous extract

Table 50

Description of 24 Hour Hi-Vol Filter Samples for Intermethod Comparison[a]

Site	Number of Filters Light	Medium	Heavy
Sacramento	1	1	1
Fresno	0	1	2
San Diego	0	2	1
San Francisco	0	3	0
Los Angeles	0	0	2
Long Beach	0	0	2
Ontario	0	1	1
Pasadena	0	0	2
Santa Ana	0	1	1
San Bernardino	0	0	2

---

a. All samples collected between 7/12/77 and 9/22/77 using Gelman EPA Grade glass fiber filters.

was analyzed successively by each method with three determinations made on separate days.

B. Results

The results, expressed as μg/ml of aqueous extract, are given in Table 51. The undiluted extracts covered the concentration range from ca. 10 to 150 μg/ml. The values shown for Method 75, Dionex IC, MRI-MTB and SulfaVer^R methods were obtained without dilution except for samples $\geq$ 85 μg/ml which were diluted by a factor of 2 before analysis. Analyses by the Colovos MTB and AIHL microchemical method employed samples diluted into the range 1-10 and 1-15 μg/ml, respectively.

The results are compared as ratios of means, relative to results by Method 75, in Table 52. Average results agreed within 10% for all methods, with all methods showing somewhat higher values, compared to Method 75. The precision of the methods with atmospheric samples is expressed by the median and range of the coefficients of variation. All methods show median C.V. values < 6%. The SulfaVer^R method showed both the highest ratio of mean and the poorest precision.

A more detailed comparison for the methods evaluated in this program is given in Figure 31. The results are nearly identical to those by comparing ratios of means since intercept values are small. All methods show slightly higher results compared to Method 75, throughout the concentration range. Except at the lowest concentrations there is little scatter in the results.

Table 51

Results of Intermethod Comparison with Atmospheric Samples (µg/ml)

Sample ID	Method 75	SulfaVer	MRI-MTB	Dionex IC	Colovos-MTB	AIHL Micro
2B	11.5 ± 0.3	13.1 ± 0.5	11.7 ± 0.5	14.0 ± 1.0	14.9 ± 0.6	13.4 ± 2.7
7D	13.5 ± 1.1	14.3 ± 1.3	12.5 ± 0.7	15.3 ± 0.8	15.1 ± 0.8	15.0 ± 1.5
1C	13.7 ± 0.3	13.5 ± 1.0	10.5 ± 1.0	14.4 ± 1.0	14.1 ± 1.2	13.7 ± 1.5
1E	16.6 ± 1.0	12.3 ± 0.3	8.0 ± 0.5	9.5 ± 1.3	13.7 ± 1.3	10.6 ± 3.8
4C	17.5 ± 1.2	15.0 ± 1.0	12.9 ± 2.0	15.3 ± 0.8	15.1 ± 0.4	15.4 ± 2.0
4A	20.6 ± 0.3	22.0 ± 2.0	21.2 ± 0.4	21.8 ± 1.5	20.4 ± 2.0	21.3 ± 2.4
2A	21.3 ± 1.3	24.2 ± 1.3	23.9 ± 4.7	24.7 ± 1.1	23.2 ± 0.9	24.2 ± 2.5
4F	22.2 ± 0.6	23.1 ± 1.6	23.0 ± 0.1	25.1 ± 1.3	24.4 ± 0.1	24.0 ± 2.5
1B	23.2 ± 0.6	25.2 ± 1.9	27.0 ± 1.6	25.3 ± 1.2	24.9 ± 0.2	25.3 ± 1.0
10D	28.8 ± 0.8	29.8 ± 2.7	28.7 ± 1.5	30.9 ± 0.2	29.4 ± 0.7	30.1 ± 1.1
2D	32.2 ± 0.9	38.1 ± 1.6	36.4 ± 0.1	36.2 ± 1.6	31.8 ± 2.5	36.4 ± 0.8
3D	35.8 ± 0.6	39.4 ± 0.9	37.6 ± 0.5	40.0 ± 1.5	37.9 ± 0.6	40.6 ± 0.1
3A	38.5 ± 0.8	41.6 ± 2.9	44.8 ± 0.8	43.2 ± 1.7	39.9 ± 4.9	43.0 ± 0.4
9F	39.2 ± 0.3	44.2 ± 0.9	43.7 ± 0.6	47.3 ± 1.4	42.0 ± 1.6	45.0 ± 0.6
7C	51.4 ± 0.6	60.3 ± 3.1	53.8 ± 1.4	54.8 ± 2.1	54.1 ± 2.1	57.6 ± 1.4
8C	53.3 ± 0.3	61.5 ± 2.2	57.6 ± 0.6	58.7 ± 0.8	55.9 ± 1.6	58.8 ± 1.0
3C	54.6 ± 0.8	59.1 ± 1.6	60.4 ± 2.2	61.4 ± 2.4	57.0 ± 2.8	59.5 ± 0.4
6G	67.8 ± 2.2	71.1 ± 0.7	70.3 ± 1.1	71.9 ± 0.8	68.9 ± 3.1	72.2 ± 1.6
10A[a]	85.8 ± 0.9	102.4 ± 3.6	89.7 ± 0.9	94.2 ± 0.9	86.6 ± 1.3	92.7 ± 2.0
5B[a]	92.4 ± 2.5	97.4 ± 5.1	103.1 ± 0.9	97.4 ± 1.1	97.5 ± 3.8	98.7 ± 0.5
6B[a]	102.8 ± 1.0	111.8 ± 7.3	106.2 ± 1.1	107.8 ± 1.4	105.9 ± 1.0	109.7 ± 2.4
9E[a]	103.5 ± 1.5	110.7 ± 6.5	111.8 ± 1.0	113.1 ± 0.7	104.2 ± 3.2	109.7 ± 2.5
5A[a]	107.9 ± 1.0	117.9 ± 6.2	113.8 ± 2.8	113.1 ± 1.8	109.1 ± 4.2	111.0 ± 0.4
8E[a]	150.0 ± 2.4	163.0 ± 2.6	153.0 ± 2.9	164.0 ± 3.1	151.1 ± 5.4	154.4 ± 1.5

---

[a] Samples diluted by factor of two before analysis by Method 75, the SulfaVer^{R}, MRI-MTB and Dionex IC methods.

Table 52

Average Agreement and Precision of Methods with Atmospheric Samples

	Ratio of Means[a]	Median C.V. (%)	Range C.V. (%)[b]
Method 75	1.00	2.2	0.6 to 8.1
SulfaVer^{R}	1.09 ± .01	5.3	1.0 to 9.1
Dionex IC	1.08 ± .01	3.9	0.6 to 13.7
MRI-MTB	1.05 ± .01	1.9	0.3 to 19.7
Colovos-MTB	1.03 ± .01	3.9	0.4 to 12.3
AIHL Micro	1.06 ± .01	2.3	0.3 to 35.8

a. Results expressed relative to those for AIHL Method 75. Errors are calculated as the standard deviation of the ratio of two dependent variables:

$$\text{S.D.}\left(\frac{x}{y}\right) = \sqrt{\text{var.}\left(\frac{x}{y}\right)} \text{ and var. } \frac{x}{y} = \left(\frac{x}{y}\right)^2 \left[\frac{\sigma_x^2}{x^2} + \frac{\sigma_y^2}{y^2} - 2\,\frac{\text{cov}(x,y)}{x \cdot y} \right]$$

b. From three determinations on each of 24 samples.

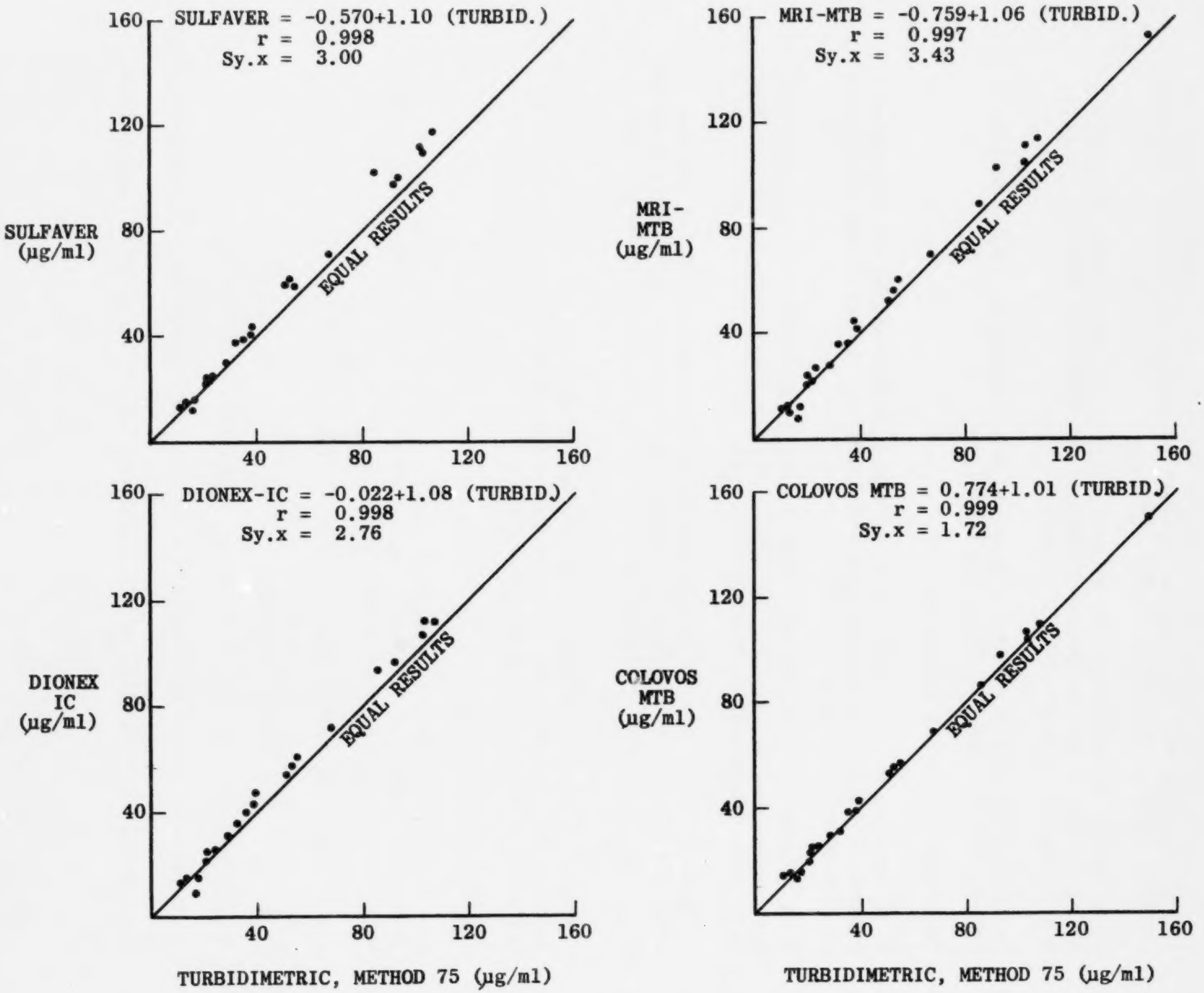


Figure 31

SCATTER DIAGRAMS OF RESULTS WITH ATMOSPHERIC SAMPLE USING FIVE SULFATE METHODS

References

1. B. R. Appel, E. L. Kothny, E. M. Hoffer and J. J. Wesolowski, Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate, Interim Report. EPA-600/2-76-059 (1976).

2. B. R. Appel, E. L. Kothny, E. M. Hoffer and J. J. Wesolowski, Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate, Final Report. EPA-600/7-77-128 (1977).

3. Selected Methods for the Measurement of Air Pollutants, Public Health Service Publication No. 999-AP-11 (1964).

4. Technicon Industrial Method 226-72W.

5. E. M. Hoffer, E. L. Kothny and B. R. Appel, Simple Method for Microgram Amounts of Sulfate in Atmospheric Particulates. Accepted for publication in Atmospheric Environment, 1978.

6. E. M. Hoffer and E. L. Kothny, A Micromethod for Sulfate in Atmospheric Particulate Matter, Air and Industrial Hygiene Laboratory Report No. 163, California Department of Health, July 1974.

7. C. Brosset and M. Ferm, "An Improved Spectrophotometric Method for the Determination of Low Sulfate Concentration in Aqueous Solutions", Swedish Water and Air Pollution Research Laboratory, 402, 24 Gothenburg, Sweden (1974).

8. Barium Chloranilate Method for Determination of Sulfates in the Atmosphere, March 1976. Prepared for U.S. EPA Environmental Monitoring and Support Laboratory, Research Triangle Park, NC.

9. Hach Chemical Company.

10. Tentative Method for the Determination of Sulfates in the Atmosphere (Automated Technicon II Methylthymol Blue Procedure) Environmental Protection Agency, Quality Assurance Branch, July 15, 1977.

11. G. Colovos, et al, Anal. Chem, 48 1693 (1976).

12. H. Small, et al, Anal. Chem. 47 1801 (1975).

13. R. T. Sheen, et al, Ind. Eng. Chem. (Anal. Ed.) 7 262 (1935).

14. Standard Methods for the Examination of Water and Waste Water, 14th Ed. (1975).

15. Brochure prepared by the Parr Co., Moline, Ill. (Circa 1900), unpublished.

APPENDIX A

AIHL Method

DETERMINATION OF SULFATE IN HIGH VOLUME PARTICULATE SAMPLES: TURBIDIMETRIC BARIUM SULFATE METHOD*

Analyte:	Sulfate	**Method No:**	61
Application:	Air Pollution	**Range:**	2 to 40 μg sulfate/m^3
Matrix:	Air	**Lower Detection Limit:**	50 μg sulfate/20 ml solution
Procedure:	Collection on filter by high-volume sampler, extraction with water followed by turbidimetric analysis	**Precision:**	5 to 11% coefficient of variation
Date First Issued:	December 1974		

Dates Revised: April 1975, February 1976 and July 1976

1. Principle of the Method

1.1 Atmospheric suspended particulate matter is collected over a 24-hour period on a 20 by 25-cm (8 by 10-inch) glass fiber filter by using a high-volume sampler. This method can also be used for samples collected on cellulose filters.

1.2 A water extract of the filter sample is treated with barium chloride to form a barium sulfate colloidal suspension. The turbidity of the suspension is measured spectrophotometrically at 500 nm.

1.3 The water extract can also be used for analysis of other water soluble species, e.g. NO_3^-, Cl^-, Na^+, NH_4^+.

---

*AIHL modification of Public Health Service Method (Ref. 1).
Underlined sentences are changed from the February 1976 revision of Method 61.
Prepared by staff of the Air and Industrial Hygiene Laboratory, State Department of Health, Berkeley, California

2. Range and Lower Detection Limit

2.1 Aliquoting is adjusted so that samples containing 2 to 40 μg sulfate/m^3 (the expected range of atmospheric samples) can be measured.

2.2 The lower detectable concentration of the turbidimetric analytical procedure is 50 μg of sulfate in 20 ml solution.

3. Interferences

3.1 Measurement is dependent upon the stability of the suspension of colloidal barium sulfate particles, size of particles, sulfate concentration, barium ion strength, pH and temperature. These parameters must be closely controlled to avoid obtaining low and inconsistent results. Addition of glycerol acts as a stabilizer for the colloid, while alcohol promotes precipitation by reducing the solubility of barium sulfate. Use of solid crystals of $BaCl_2$ eliminates the problem of barium ion strength and solution aging. Sulfate concentration is maintained within the limits of the method, and pH is controlled by addition of dilute HCl. Variations in temperature between 20 to 30°C do not appear to have a significant effect. Vigorous shaking of the solution during the addition of barium chloride promotes the formation of finer particles that stay in suspension longer.

3.2 Sulfur-containing anions are generally strong positive interferents probably due to air oxidation to sulfate. Colloidal clay interferes strongly but in a direction apparently dependent on the sulfate/interferent ratio. Table 1 summarizes results of a recent AIHL study (ref. 2).

3.3 Glass fiber filters are not sulfate free. The amount of sulfate depends on the manufacturer's filter types and lots. For example, the MSA Type 1106 BH

3. (cont)

filters have been found to contain up to 4 mg sulfate per 20 by 25-cm sheet. This sulfate can be removed by water wash prior to sampling if desired. When this is not practical, as is the case for many monitoring purposes, determine the background sulfate concentration (section 7.3.6) for every lot and type of sampling filter used and correct the results accordingly.

3.4 Frequently the aqueous extract containing the sulfate shows background coloration and/or turbidity which may interfere with the analysis. These interferences are accounted for by measuring the absorbance (A_1) of the filtrate and glycerol-alcohol-acid mixture before the addition of the barium chloride. This value is subtracted from the absorbance (A_2) of the sample after the addition of barium chloride.

4. Precision and Accuracy

4.1 The precision of the method was established at AIHL by three determinations on each of the extracts from 12 high-volume atmospheric samples (ref. 2). Extracts were diluted into the optimal concentration range of the method. Under carefully controlled conditions, a coefficient of variation of 5% was found. This compares to the value 5% given in ASTM method D516 (ref. 3) and to the value 11% reported in the Public Health Service method (ref. 1).

4.2 The extraction efficiency of the analytical method was recently evaluated at AIHL utilizing exhaustive extraction of ten 24-hour samples collected in Southern California. The mean recovery was 96.1 ± 1.2%.

4. (cont)

Also MSA 1106 BH and Staplex TFA 810 filters were spiked with known amounts of sulfate salts and recoveries close to 100% were established.

5. Equipment

5.1 High-volume sampler. A motor blower filtration system with a sampling head which can accomodate a 20 by 25-cm glass fiber filter and capable of sampling at an initial flow rate of about 1.7 m^3/min (60 ft^3/min).

5.2 Filters. Use 20 by 25-cm (8 by 10-inch) glass fiber filters of low sulfate content.

5.3 Refluxing Apparatus. Use 125 ml flask with ground glass joint, a reflux condenser and a hot plate.

5.4 Filtering Funnel and Whatman No. 42 filter paper.

5.5 Cuvettes. Matched 20 mm or 1 inch cuvettes.

5.6 Pipettes. Use 20, 5 ml and other sizes as required.

5.7 Spectrophotometer. Capable of measuring at 500 nm with a bandpass of 16 nm or less.

5.8 Filtrate Receivers. 100 ml glass-stoppered graduated cylinders.

6. Reagents

All reagents should be made from ACS analytical-grade chemicals.

6.1 Hydrochloric acid (10 N). Add carefully 80 ml of concentrated hydrochloric acid to 20 ml of distilled water in 100 ml glass stoppered graduate cylinder and dilute to mark with water.

6.2 Glycerol - alcohol - acid solution. Mix 20 ml of glycerol with 40 ml of reagent grade 95% ethyl alcohol and 15 ml of 10 N HCl.

Caution: Do not use denatured alcohol.

6. (cont)

6.3 Barium chloride. $BaCl_2 \cdot 2\ H_2O$ Crystals, 20-30 mesh. J. T. Baker Cat. No. 0974 or equivalent.

6.4 Standard sulfate solution (100 μg sulfate/ml). Dry anhydrous sodium sulfate at 105°C for 4 hours and cool in a desiccator. Dissolve 0.148 g of the dried anhydrous sodium sulfate in distilled water and dilute to 1 liter. This solution contains 100 μg sulfate per ml.

7. Procedure

7.1 Sampling. Using the high-volume sampler, collect the particulate matter from approximately 2,000 m^3 of air. Twenty-four hours is the usual sampling period. Note and record the airflow rates at the start and end of the sampling period.

7.2 Sample Preparation - The sample filter should be delivered to the laboratory unfolded in a glassine envelope. An aliquot of the filter is taken for analysis. (Appendix 1 discusses sectioning the filter for various analyses). One-fourth of the filter (Quadrant A as shown in Appendix 1) is cut into about 5-cm lengths for ease in handling and placed into the 125 ml boiling flask containing 50 ml of distilled water. The sample is refluxed for 60 minutes. The hot solution is filtered through a Whatman No. 42 filter paper which has been previously rinsed free of sulfate with at least 50 ml of boiling distilled water. The filtrate is collected in a 100 ml glass-stoppered graduated cylinder. Both the boiling flask and

7. (cont)

sample filter are rinsed 3 times with about 10 ml each of boiling distilled water. After cooling, the final filtrate volume is brought up to 100 ml with distilled water.

7.3 Analytical Procedure

7.3.1 Pipette an aliquot of the filtrate, normally 20 ml, containing 50 to 1000 μg sulfate into a clean dry 25 ml glass stoppered graduate cylinder. When a smaller aliquot is used, dilute to 20 ml with distilled water. Add 5 ml of the glycerol-alcohol-acid solution and mix.

7.3.2 Pour a portion of the solution in a dry cuvette. Determine the absorbance at 500 nm against distilled water and record as A_1.

7.3.3 Pour the sample solution in the sample cuvette back in the cylinder. Add approximately 0.25 g of barium chloride crystals, stopper the flask and shake it vigorously for 45 seconds to dissolve the crystals.

7.3.4 Let the sample stand for exactly 40 minutes at room temperature (20° to $30^\circ C$). Then gently mix the suspension by inverting the graduated cylinder once and measure the absorbance (A_2) of the solution against distilled water as above. When large number of samples are to be analyzed, add the $BaCl_2$ crystals at timed intervals (e.g. 1 min) with similar intervals between spectrophotometer readings.

7.3.5 Analyze a standard sulfate solution as a control with each batch

7. (cont)

of samples to detect gross variations in the analysis. Deviations up to 5% from the standard curve are acceptable.

7.3.6 A correction for the background concentration of sulfate in the filters must be made for each new lot of filters. This value (B) must be the average of at least 5 determinations using 5 filters from each lot of 100 filters using the entire analytical procedure (sections 7.2 and 7.3) and must be subtracted as filter blank (section 9.2).

8. Standards and Calibration

8.1 Prepare standard from the 100 μg sulfate/ml standard solution by pipetting respectively 0, 0.5, 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, and 10.0 ml into 25 ml glass stoppered graduated cylinders. Bring the volumes to 20 ml with distilled water. Analyze the standard solutions as in section 7.3, but the determination of A_1 is unnecessary since negligible values are always obtained.

8.2 Plot the absorbance readings (A_2) on the vertical axis versus the corresponding μg of sulfate on the horizontal axis using a rectilinear graph paper.

8.3 The relation between absorbance and amount of sulfate should be linear between 300 and 1000 μg. The slope of the curve in this range is calculated by least squares and used in determining the amount of sulfate in each sample. Below 300 μg, the relationship is non-linear and the sulfate concentration must be determined graphically.

9. Calculations

9.1 Air volume calculation

a. For samples collected at altitudes less than 2000 feet above mean sea level, use the calibrated air flow rate, which is approximately equal to the flow rate under standard conditions of 760 Torr and 25°C.

b. For samples collected at altitudes of 2000 feet or greater, calibrate the high-volume sampler using the APB procedure (4) which corrects the flow rate to standard sea level conditions.

c. Using the flow rate determined in (a) or (b) above, calculate the air volume from the sampling time and the average of the airflow rates at the start and end of the sampling period.

$$V = \frac{Q_1 + Q_2}{2} \times t$$

Where: Q_1 = airflow rate at start of sampling period (m^3/min)

cubic feet per minute x 0.02832 = m^3/min

Q_2 = airflow rate at end of sampling period (m^3/min)

cubic feet per minute x 0.02832 = m^3/min

t = sampling period (min)

V = sample volume in cubic meters (m^3) at standard conditions

9.2 Subtract A_1 from A_2 and, calculating from the calibration curve obtained in section 8, determine the equivalent μg of sulfate (C) in the aliquot. Calculate the concentration of sulfate in the 20 by 25 cm filter sample in $\mu g/m^3$ as follows:

9. (cont)

$$\mu g \text{ sulfate}/m^3 = \frac{(F_1 \times F_2 \times C) - B}{V}$$

Where: $F_1 = \frac{\text{total ml of filtrate}}{\text{ml of filtrate taken for analysis}}$

$F_2 = \frac{\text{total sample area of filter sample}}{\text{sample area of filter quadrant analyzed}}$

C = µg sulfate in aliquot of sample taken

B = µg sulfate/20 x 25-cm filter blank

V = air sample volume in m^3 (determined as in ¶ 9.1.)

10. References

1. Public Health Service Publication No. 999-AP-11, Selected Methods for the Measurement of Air Pollutants; "Determination of Sulfate in Atmospheric Suspended Particulates: Turbidimetric Barium Sulfate Method", pp I-1, U. S. Dept. of Health, Education & Welfare, PHS, Div. of Air Pollution, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio 45226, May 1965.
2. Final Report, EPA Contract No. EPA 68-02-1660, "Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate", B.R. Appel, E.L. Kothny, E.M. Hoffer and J.J. Wesolowski, February 1976.
3. ASTM Method D516-68 (Method B), "Standard Methods of Test for Sulfate Ion in Water and Waste Water"; 1975 Book of ASTM Standards; Part 31; Water, ASTM; Philadelphia, PA.
4. Standard Procedure for the Calibration of Hi-Vol Samplers and Plotting of Flow Calibration Curves Corrected for Altitude, California Air Resources Board, Sept. 1975, Sacramento, California.

Appendix 1

Cutting of Glass-Fiber High-Volume Filters

1. Remove the glass-fiber filter from the shipping envelope.

2. Using a clean cutting tool, preferably stainless steel, cut the filter in half. Then cut one half into two equal quadrants as shown in Figure 1.

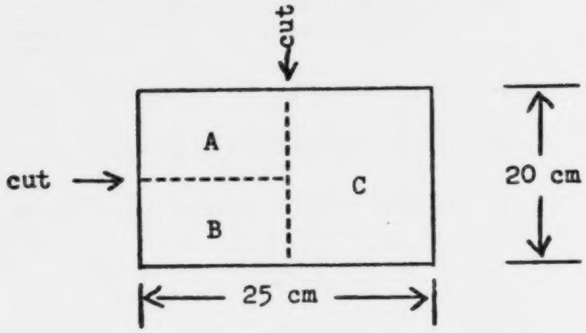


Figure 1

3. Use quadrant "A" for the determination of sulfate (AIHL Method 61) and nitrate (AIHL Method 66).

4. Use quadrant "B" for the determination of lead (AIHL Method 54).

5. Use half "C" for the determination of benzene-soluble organics (AIHL Method 67).

Table 1

The Effect of Potential Interferents in the $BaCl_2$ Turbidimetric Method[a]

Interferent	Sulfate/Interferent Ratio[b] 2:1 (w/w)	 0.66:1 (w/w)
Sulfide	++	++
Sulfite	++	++
persulfate	0	++
thiosulfate	++	++
bicarbonate	+	0
phosphate	0	0
silicate	0	0
calcium	0	0
lead	+	0
colloidal clay	-	++
p-benzoquinone (a yellow chromophore used to simulate a yellow extract)	0	0

a. + indicates > 10% increase in sulfate

++ indicates > 25% increase in sulfate

- indicates > 25% decrease in sulfate

0 indicates < 10% change in sulfate

b. sulfate concentration 20 μg/ml

Source: Ref. 2

METHOD 61. TURBIDIMETRIC SULFATE - ADDENDUM

1. Limit of Detection

The method specifies that the lower detection limit is 50 μg per aliquot. This corresponds to a net absorbance of 0.03, i.e., $A_2 - A_1$. Since A_1 may be as large as 0.07, the chemist and section leader should carefully examine any A_2 value smaller than 0.10 absorbance units, with the thought that the net absorbance may be less than the limit of detection. In any case, all $A_2 - A_1$ values of 0.03 units or less should be considered as being less than 50 μg sulfate.

2. Range of the Method

The range of the method is given as 2 to 40 $\mu g/m^3$, equivalent to 200 to 4000μg per aliquot. Actually, the curve is linear between 300 and 1500 μg sulfate, corresponding to absorbances from 0.10 to 0.90. (Note that the standards described in Method 61 do not cover this range. It should be modified to include 1200 and 1400 μg standards.) The optimum reading, from an instrumental standpoint, is 0.40 absorbance units. The following protocol should be adopted:

a. Aliquots shall be adjusted to an A_2 value of 0.40. Samples giving A_2 values less than 0.10 or greater than 0.90 must be rerun, using an appropriate aliquot size.

b. Standards greater than 1500 μg shall not be run, since they adversely affect the linear regression line.

c. Chemists shall not record, as a reportable result, $A_2 - A_1$ values > 0.90 nor < 0.10, unless in the latter case, a 20 ml aliquot was used.

3. Analytical Procedure

There should be no deviation from the written procedure. If circumstances should require the section leader to temporarily modify the procedure, he should instruct the chemist to flag these results and should, by memo, explain the circumstances to his group leader, the QA chairman and the data handling section.

This memo should be attached to, and become a part of, the chemist's and section leader's copy of Method 61.

APPENDIX B

AIHL Method

DETERMINATION OF SULFATE IN HIGH VOLUME PARTICULATE SAMPLES: SIMPLIFIED AND IMPROVED TURBIDIMETRIC BARIUM SULFATE METHOD*

Analyte:	Sulfate	Method No:	75
Application:	Air Pollution	Working Range:	140 to 1400 µg sulfate/20 ml
Matrix:	Air	Detection Limit:	50 µg sulfate/20 ml solution
Procedure:	Collection on filter by high-volume sampler, extraction with water followed by turbidimetric analysis	Precision:	≤ 6% coefficient of variation in working range
Date First Issued:	September 1978	Accuracy:	Within 4%, on average, using EPA Audit Strips

1. Principle of the Method

1.1 Atmospheric suspended particulate matter is collected over a 24-hour period on a 20 by 25-cm (8 by 10-inch) filter by using a high-volume sampler.

1.2 A water extract of the filter sample is treated with barium chloride to form a barium sulfate colloidal suspension. The turbidity of the suspension is measured spectrophotometrically at 500 nm.

1.3 Results are dependent upon the stability of the suspension of colloidal barium sulfate, particle size, barium chloride crystal and aggregate size, pH and temperature. Glycerol acts as a stabilizer for the colloid while alcohol promotes precipitation by reducing the solubility of barium sulfate.

1.4 Barium sulfate formation and turbidity measurement are done in test tubes, thereby eliminating all sample transfers.

---

*The procedure was developed by E. M. Hoffer and is a revised version of AIHL Method 61. Evaluation of the procedure is given in Reference 1.

Prepared by staff of the Air and Industrial Hygiene Laboratory, State Department of Health Services, Berkeley, California.

2. Range and Detection Limit

2.1 The detection limit concentration of this turbidimetric analytical procedure is 50 μg of sulfate in 20 ml solution. The working range is from 140 to 1400 μg sulfate/20 ml solution.

3. Interferences

3.1 Variations in temperature between 20 to 30°C do not appear to have a significant effect.

3.2 Sample coloration and/or turbidity may interfere with the analysis. These interferences are minimized by measuring the absorbance (A_1) of the filtrate plus glycerol-alcohol-acid mixture before the addition of the barium chloride. This value is subtracted from the absorbance (A_2) of the sample after the addition of barium chloride. In spite of this correction, interference may persist. Colloidal clay, used to simulate the source of turbidity in some samples, is a strong negative interferent. Yellow, water-soluble organics, isolated from atmospheric particulate matter, show a small negative interference at low sulfate concentration (Table 1).[1]

3.3 Sulfur-containing anions are generally strong positive interferents probably due to air oxidation to sulfate[2].

3.4 Glass fiber filters contribute to observed sulfate both from a "blank" value and by artifact sulfate formation[2]. Artifact sulfate can be minimized by employing pH neutral filters (e.g. quartz fiber). With all filter types, the background or blank sulfate concentration should be measured (Section 8.3.3) for every lot and type of sampling filter used and the results corrected.

4. Precision and Accuracy

4.1 The precision of the method was established by three determinations on each of the extracts from 24 high-volume atmospheric samples ranging in concentration from 240 to 1500 μg sulfate per 20 ml solution. The median coefficient of variation was 2.2% (range 0.6 to 8.1%). This compares to the value 5% given in ASTM method D516[3] and to the value 11% reported in the Public Health Service method.[4]

4.2 Accuracy was established by analyzing EPA audit strips (i.e. filter strips loaded with known quantities of sulfate). For solutions in the range 300 to 1700 μg/20 ml, the ratio of observed to theoretical concentration ranged from 1.00 to 1.05 with mean value 1.04.

5. Working Range

5.1 Working range is defined as the sulfate concentration range providing approximately constant coefficient of variation and "relative accuracy". The latter indicates the accuracy of the method relative to the value obtained in the optimal concentration range of the method. This is determined using a pooled, concentrated atmospheric sample extract, diluted to varying degrees.

5.2 This procedure yielded a relative accuracy within 7% in the concentration range 140 to 1400 μg sulfate/20 ml solution with a C.V. of $\leq$ 6%.

6. Equipment

6.1 High-volume sampler. A motor blower-filtration system with a sampling head which can accomodate a 20 by 25-cm filter and capable of sampling at an initial flow rate of about 1.7 m^3/min (60 ft^3/min).

6.2 Filters. 20 by 25-cm (8 by 10-inch) filters.

6.3 Ultra Sonic bath. For example, Bransonic Model 32.

6.4 Fine glass frit, 30 ml capacity

6.5 Fisher filtrator

6.6 25 x 150 mm Teflon-lined screw capped test tubes. The tubes must be unscratched. Add a fiduciary mark to permit reproducible positioning in the spectrophotometer. Test tubes are further pre-selected as follows: a) fill all test tubes with distilled water, b) using a single beam spectrophotometer, select any tube for an initial reference and determine the tube with highest % T, c) label this tube and use as blank for all sample determinations, and d) match all other test tubes with the blank within 2%.

6.7 Pipettes. 20, 5 ml and other sizes as required.

6.8 Spectrophotometer. Capable of measuring at 500 nm with a bandpass of 20 nm or less, using 1 inch cells.

6.9 Filtrate receivers. 60 or 100 ml plastic bottles with tightly fitting caps.

7. Reagents

Make all reagents from ACS analytical-grade chemicals.

7.1 Hydrochloric acid (10 N). Add carefully 80 ml of concentrated hydrochloric acid to 20 ml of distilled water in 100 ml glass stoppered graduate cylinder and dilute to mark with water.

7.2 Glycerol-alcohol-acid solution. Mix 20 ml of glycerol with 40 ml of reagent grade 95% ethyl alcohol and 15 ml of 10 N HCl. This solution is stable for up to 6 months. Caution: Do not use denatured alcohol.

7.3 Barium chloride. $BaCl_2 \cdot 2H_2O$, 20-30 mesh if available. Reference 1 details an evaluation of barium chloride mesh and crystal size, both of which influence the calibration curve. In general, use of $BaCl_2 \cdot 2H_2O$ not graded for turbidimetric analysis yields a calibration curve with reduced slope and increased scatter.

7.4 Standard sulfate solution (100 µg sulfate/ml). Dry anhydrous sodium sulfate at 105°C for 4 hours and cool in a desiccator. Dissolve 0.148 g of the dried sodium sulfate in distilled water and dilute to 1 liter. This solution contains 100 µg sulfate per ml.

8. Procedure

8.1 Sampling. Using the high-volume sampler, collect the particulate matter from approximately 2,000 m^3 of air. Twenty-four hours is the usual sampling period. Note and record the airflow rates at the start and end of the sampling period.

8.2 Sample Preparation. The sample filter should be delivered to the laboratory unfolded in a glassine envelope. Take an aliquot of the filter for analysis. (Appendix 1 discusses sectioning the filter for various analyses). Cut one-fourth of the filter (Quadrant A as shown in Appendix 1) into about 5-cm lengths for ease in handling. Place it in a 50 ml glass stoppered Erlenmeyer flask containing 50 ml of distilled water and then in an ultrasonic bath for 30 minutes. A batch of 18 samples may conveniently be handled at once. Filter the solution through a clean, fine porosity fritted glass filter (30 ml volume) into a 60 ml polyethylene bottle using a Fisher filtrator. After discarding filter pulp, carefully wash the frit free of sulfate with distilled water and suction it dry. Washings are not added to the extract.

8.3 Analytical Procedure

8.3.1 Pipet aliquots of the filtrates, normally 20 ml, into a series of clean and dry screw capped test tubes. When a smaller aliquot is used, dilute to 20 ml with distilled water. Add 5 ml of the glycerol-alcohol-acid solution and mix slowly, inverting a batch of samples 6 times, taking about 2 seconds to invert, and waiting about 10 seconds before re-inverting. Wait 10 minutes to permit escape of bubbles.

8.3.2 Determine the absorbance at 500 nm against distilled water and record as A_1.

8.3.3 Add one scoop (approx. 0.25 g) of barium chloride crystals at one minute intervals to the batch of samples, following each addition by mechanical shaking. After adding $BaCl_2$ to the first sample, cap tightly and shake for 60 seconds at 90 oscillations/minute on an Eberhard (or equivalent) shaker, with the tube lying on the plane of oscillation. While shaking the first sample, time the addition of the $BaCl_2$ to the second sample and, when shaking of the first is complete, immediately shake the second. Continue in this way for all samples.

8.3.4 Let the first sample stand at 20 to 30°C for exactly 40 minutes from the time of the initial $BaCl_2$ addition. Then, gently mix the suspension by inverting the sample test tube once and measure the absorbance (A_2) of the solution against distilled water as above. Read each successive sample at 60 second intervals to give each sample 40 ± 1 minutes standing time.

8.3.5 A correction for the background concentration of sulfate in the filters must be made for each new lot of filters. This value (B) must be the average of at least 5 determinations using 5 filters from each lot of 100 filters using the entire analytical procedure (Sections 8.2 and 8.3) and must be subtracted as filter blank (Section 10.2).

9. Standards and Calibration

9.1 For each batch of samples, prepare calibrating solutions using the 100 µg sulfate/ml standard solution. Pipet 0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0 and 14 ml into separate test tubes and bring the volumes to 20 ml with distilled water. Analyze the calibrating solutions as in Section 8.3.

9.2 Plot the difference in absorbance readings (A_2-A_1) on the vertical axis versus the corresponding µg of sulfate on the horizontal axis using a rectilinear graph paper.

The relation between absorbance and amount of sulfate should be approximately linear between 300 and 1000 µg/20 ml. By restricting samples to this range, linear regression can be employed.

For analyses in the range 140 to 1400 µg/20 ml, a third order regression equation is used of the form $y = a + bx + cx^2 + dx^3$ where x = µg/20 ml sulfate and y = absorbance.

10. Calculations

10.1 Air Volume Calculation

a. For samples collected at altitudes less than 2000 feet above mean sea level, use the calibrated air flow rate, which is approximately equal to the flow rate under standard conditions (760 Torr and 25°C).

b. For samples collected at altitudes of 2000 feet or greater, calibrate the high-volume sampler using the ARB procedure[5] which corrects the flow rate to standard sea level conditions.

c. Using the flow rate determined in (a) or (b) above, calculate the air volume from the sampling time and the average of the airflow rates at the start and end of the sampling period.

$$V = \frac{Q_1 + Q_2}{2} \times t$$

Where: Q_1 = airflow rate at start of sampling period (m^3/min)

cubic feet per minute x 0.02832 = m^3/min

Q_2 = airflow rate at end of sampling period (m^3/min)

cubic feet per minute x 0.02832 = m^3/min

t = sampling period (min)

V = sample volume in cubic meters (m^3) at standard conditions

10.2 Subtract A_1 from A_2 and, calculating from the regression equation obtained in Section 8, determine the equivalent μg of sulfate (C) in the aliquot. Calculate the concentration of sulfate in the 20 by 25 cm filter sample, in μg/m^3 as follows:

$$\mu g\ sulfate/m^3 = \frac{(F_1 \times F_2 \times C) - B}{V}$$

Where: $F_1 = \frac{\text{total ml of filtrate}}{\text{ml of filtrate taken for analysis}}$

$F_2 = \frac{\text{total sample area of filter sample}}{\text{sample area of filter quadrant analyzed}}$

C = μg sulfate in aliquot of sample taken

B = μg sulfate/20 x 25-cm filter blank

V = air sample volume in m^3 (determined as in Sec. 10.1)

11. References

1. Final Report, EPA Grant No. 805-447-1 "Improvement and Evaluation of Methods for Sulfate Analysis", B. R. Appel, E. M. Hoffer, M. Haik, W. Wehrmeister, E. L. Kothny and J. J. Wesolowski, 1978.

2. Final Report, EPA Contract No. EPA 68-02-1660, "Comparison of Wet Chemical and Instrumental Methods for Measuring Airborne Sulfate", B. R. Appel, E. L. Kothny, E. M. Hoffer and J. J. Wesolowski, February 1976.

3. ASTM Method D516-68 (Method B), "Standard Methods of Test for Sulfate Ion in Water and Waste Water", 1975 Book of ASTM Standards, Part 31, Water, ASTM, Philadelphia, PA.

4. Public Health Service Publication No. 999-AP-11, Selected Methods for the Measurement of Air Pollutants; "Determination of Sulfate in Atmospheric Suspended Particulates: Turbidimetric Barium Sulfate Method", pp. I-1, U.S. Dept. of Health, Education and Welfare, PHS, Div. of Air Pollution, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio 45226, May 1965.

5. Standard Procedure for the Calibration of Hi-Vol Samplers and Plotting of Flow Calibration Curves Corrected for Altitude, California Air Resources Board, September 1975, Sacramento, California.

Appendix 1

Cutting of Glass-Fiber High-Volume Filters

1. Remove the filter from the shipping envelope.
2. Using a clean cutting tool, preferable stainless steel, cut the filter in half. Then cut one half into two equal quadrants as shown in Figure 1.

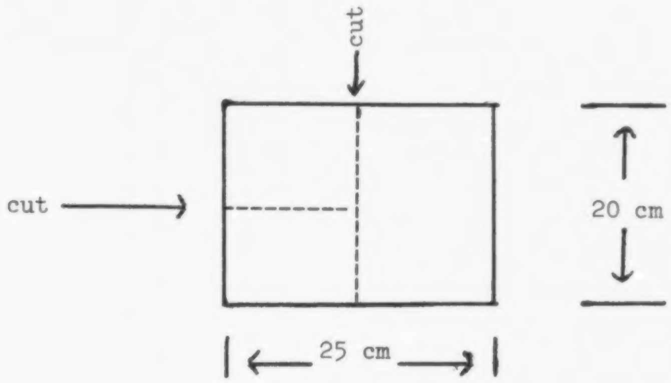


Figure 1

3. Use quadrant "A" for the determination of sulfate.

Table 1

Interference Effect with the AIHL Method 75 (μg/ml Observed Sulfate)[a]

Sulfate Level μg/ml	10				35				60			
Interferent Level[b]	A	B	C	D	A	B	C	D	A	B	C	D
Interferent												
Colloidal clay	8.8 1.6	5.2 2.3	1.6[c] ---	2.9[d] 1.0	35.3 0.5	33.2 0.3	31.2 0.2	30.0 0.6	58.3 0.9	56.2 1.2	53.0 0.7	50.7 0.7
Organics	9.4 0.9	9.9 0.3	9.4 0.3	8.3 0.3	35.4 1.9	35.8 0.5	35.2 0.7	35.2 0.4	60.0 0.7	60.5 0.5	59.0 1.1	59.1 2.4
bicarbonate (HCO_3^-)	10.2 0.2	10.1 0.7	10.0 0.6	10.4 0.3	37.0 0.3	36.1 0.2	36.5 0.5	36.0 0.6	60.0 0.3	59.5 0.9	60.2 0.8	60.0 0.6

a. Mean of three determinations, third order regression, with ± 1 σ values shown below mean.

b. Interferent concentrations:

	A	B	C	D
Colloidal clay (μg/ml)	10	25	50	75
Organics (Abs/cm at 400 nm)	0.0125	0.025	0.05	0.1
bicarbonate (μg/ml)	3.8	7.5	15	30

c. Single value. Two trials yielded negative results.

d. Mean of two results. One value yielded negative results.

PROTOCOL FOR THE RUGGEDNESS TEST FOR DETERMINATION OF SULFATE BY THE TURBIDIMETRIC METHOD

Introduction

Ten factors were selected to evaluate as variables in conducting the $BaSO_4$ turbidimetric method. The factors and the levels of each variable to be studied are shown in Table C-1. In all trials, standard quantities of sulfate are to be added to the samples to permit analysis in the approximately linear region of the working curve.

The ruggedness test is designed to determine the sensitivity of the method to variation in each of the factors studied, following AIHL Method 61.

Experimental Plan

The design is a balanced incomplete block as described by Plackett and Burman, with 12 runs for the ruggedness test, and three replicates for each run. Each run will have 10 factors and a dummy factor, and each factor may be either of two levels. The scheme for all runs is shown in Table C-2 with the level of each factor designated by a "+" or "-" as previously defined in Table C-1.

A standard calibration curve with six points ranging from 300 μg SO_4/10 ml - 2000 μg SO_4/10 ml, plus 10 ml of water for each point was included for each run. Following the design in Tables 1 and 2, half of the runs were read with a B&L 70 spectrophotometer and a 20 mm cell, and the other half, with a B&L 20 and 25.4 mm cell.

Table C-1

FACTORS FOR EVALUATION IN RUGGEDNESS TEST

	Low (-)	High (+)
A = Level of $SO_4^=$	100 µg/10 ml	1000 µg/10 ml
B = Level of Addition of $SO_4^=$	300 µg/10 ml	600 µg/10 ml
C = Age of Reagent Mixture	New (0-1 mo.)	Old (2 years)
D = Varying Strength of Reagent Mixture	(4 ml + 1 ml of 95% ethanol)	5 ml
E = Time After Adding Reagent Mixture Until Mixing	1 min.	10 min.
F = Mixing before Absorbance Reading 1[c,d]	Gentle Mixing[e]	Vigorously for 20 sec.
G = Addition of $BaCl_2$	½ scoop (ca. 0.125 g)	1 scoop (ca. 0.25 g)
H = Mode of Shaking, after Addition of $BaCl_2$	Gently for 45 sec. (1 shake/second)	Vigorously for 45 sec.
I = Timing before Second Absorbance Reading[a]	20 min.	40 min.
J = Spectrophotometer, cell length and mode of mixing[b]	B & L 20, 25.4 mm separate cells	B & L 70, 20 mm graduated cylinder
K = Dummy	-	+

---

a. Following $BaCl_2$

b. Sample and reagents mixed either in separate cells used for turbidity readings or in graduated cylinders with tranfers to a single 20 mm cell for reading turbidity.

c. The absorbance due to initial turbidity of sample plus the glycerin-alcohol-HCl "mixed" reagent before addition of $BaCl_2$.

d. After transfer of solution to cuvet, entrapped bubbles can cause appreciable error in absorbance.

e. Slowly add glycerol-alcohol-acid solution minimizing air entrainment. Mix solution by inverting graduated cylinder slowly (about 2 seconds to invert). After 10 seconds, invert again. Repeat for total 6 inversions.

Table C-2

DESIGN OF RUGGEDNESS TEST[a]

Run/Factor	A	B	C	D	E	F	G	H	I	J	K
1	+	+	-	+	+	+	-	-	-	+	-
2	+	-	+	+	+	-	-	-	+	-	+
3	-	+	+	+	-	-	-	+	-	+	+
4	+	+	+	-	-	-	+	-	+	+	-
5	+	+	-	-	-	+	-	+	+	-	+
6	+	-	-	-	+	-	+	+	-	+	+
7	-	-	-	+	-	+	+	-	+	+	+
8	-	-	+	-	+	+	-	+	+	+	-
9	-	+	-	+	+	-	+	+	+	-	-
10	+	-	+	+	-	+	+	+	-	-	-
11	-	+	+	-	+	+	+	-	-	-	+
12	-	-	-	-	-	-	-	-	-	-	-

[a] Plus and minus indicate levels of variable as given in Table C-1.

Data Evaluation

Since the runs involve the deliberate addition of sulfate in each case, the result for a given run is considered to be:

Run Result = Sulfate (observed)/Sulfate (expected)

The effect of variation of a given factor (e.g. A) over the range corresponding to the "+" and "-" levels is determined by subtracting the mean of all runs with "-" values for A from the mean results of all runs with "+" values for A:

$$\text{Effect of A} = \frac{\text{Run }(1,2,4,5,6,10)}{6} - \frac{\text{Run }(3,7,8,9,11,12)}{6}$$

For evaluation, the following steps will be used:

1. Rank the effects (highest first)
2. Sum the variance (i.e., square of the effect) and calculate the % of the variance in the turbidimetric method due to each factor.

Quality Assurance

The addition of standard amounts of sulfate to a sample, while permitting use of the nearly linear portion of the working curve, introduces a potential error because of imprecision and/or inaccuracy in pipetting the standard addition. For example, a 1% error in pipetting 300 μg sulfate leads to an error of about 8% for a sample initially containing 40 μg sulfate. Accordingly, careful calibration of the volumetric equipment is essential.

The standard addition/10 ml and the addition of the 10 ml of water and the mixed reagent are added by Repipet[*], while the level of sulfate of 100 μg/10 ml and 1000 μg/10 ml are by conventional pipet. The various concentrations of standard sulfate for the turbidimetric calibration curve are also pipetted with a volumetric 10 ml pipet. The standard addition/10 ml was calibrated by weighing the 10 ml that are expelled by the Repipet. The Repipet was adjusted to dispense 300 or 600 μg $SO_4^=$/10 ml with an accuracy of ± 0.5%.

---

[*] A device which attaches to a reagent bottle permitting variable and reproducible dispensing of calibrated volumes of reagent.

Bibliography

1. Plackett and Burman, "The Design of Optimum Multifactorial Experiments", Biometrika 33, 305 (1946).

2. "Efficient Screening of Variables", Stowe and Mayer, Ind & Eng Chem 58: No. 2, 36 (1966).

3. "Statistical Techniques for Collaborative Tests", published by A.O.A.C. (1973).

4. "Measurement of Atmospheric Sulfates: Evaluation of the Methylthymol Blue Method", EPA-600/4-76-015, March 1976.

GLOSSARY

S_n = observed sulfate sample in experimental run including the level of sulfate from a standard or field sample plus the standard addition for the run.

$S_{n.1}$, $S_{n.2}$, $S_{n.3}$ = observed sulfate values for 3 replicates for Run n.

$\overline{S}_n$ = average sulfate values from 3 replicates for Run n.

A_n = standard addition for run n calibrated by weighing solution at ambient temperature.

$A_{n.1}$, $A_{n.2}$, $A_{n.3}$ = standard addition for three trials for Run n.

$\overline{A}_n$ = average of standard additions for three trials for Run n.

Ks_n = calculated value for the level of sulfate and standard addition for Run n (factors A plus B in Table 1).

R_n = result for Run n as obtained by subtracting calculated sulfate from that observed:

$$R_n = \overline{S}_n - Ks_n$$

Protocol for SulfaVer IV Procedure

1. Determine initial transmittance (T_1) of sample in a 2 cm cuvet at 500 nm using a B and L 70 Spectrophotometer.

2. Tap SulfaVer IV pillows to settle contents. Cut off tops and carefully transfer contents simultaneously to a set of 12 samples and/or standards contained in 25 x 150 mm Teflon-lined screw cap test tubes. Simultaneous transfer can be facilitated by using a tray in which pillows are clipped at intervals corresponding to the space between test tubes. Inverting the tray thereby empties contents of each pillow into a row of test tubes. A set of standards is run daily.

3. Tighten caps on each, mount horizontally on a mechanical shaker which oscillates in a horizontal plane (e.g., as supplied by Eberbach Corp., Ann Arbor, MI) and shake for one minute at 90 oscillations per minute.

4. Return samples to a rack in a vertical position and allow to stand for 20 minutes.

5. Transfer to a 2 cm cuvet and read transmittance (T_2). Reading a set of 12 samples and/or standards requires 6 minutes or less.

6. To reduce analysis time a second set of 12 samples can be started during the 20 minute reaction time.

TENTATIVE METHOD FOR THE DETERMINATION OF SULFATES IN THE ATMOSPHERE (AUTOMATED TECHNICON II METHYLTHYMOL BLUE PROCEDURE)

A tentative method is one which has been carefully drafted from available experimental information, reviewed editorially within the Quality Assurance Branch, and has undergone extensive laboratory evaluation. The method is still under investigation and therefore, is subject to revision.

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

March 1978

1. Principle and Applicability

1.1. Ambient sulfates are collected by drawing air through a glass fiber filter with a high volume pump. The filters are extracted with water sonically or by refluxing and the extract is treated with barium chloride and methylthymol blue (MTB) at a pH of 2.8. After the barium sulfate precipitates, the pH is increased to 12.4 and the unreacted barium forms a chelate with the MTB. The uncomplexed MTB remaining is then measured colorimetrically at 460 nm.[1/]

1.2. The method is applicable to the collection of 24-hr samples in the field and subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1. The range of the analysis is 3 to 95 $\mu g\ SO_4^{=}/ml$. With a 50-ml extract from one-twelfth of the high volume filter collected at a sampling rate of 1.7 m^3/min (60 cfm) for 24 hr, the range of the method is 0.74 to 23.3 $\mu g/m^3$. The lower range may be extended up to 12-fold by increasing the portion of the filter extracted. The upper limit may be increased by diluting the sample with distilled water.

2.2. Using the procedure outlined, a concentration of 3 $\mu g\ SO_4^{=}/ml$ will produce a scale deflection of 3% of full scale (signal/noise ratio of 2).

3. Interferences

3.1. Sulfides, sulfites, and phosphates produce a positive interference which is dependent on the concentration of sulfate and the interfering ion.

3.2. The interferences from cations are eliminated by passing the sample through an ion-exchange column.

4. Precision and Accuracy

4.1. A single laboratory's relative standard deviation based on the analyses of duplicate strips taken from several thousand filter samples is ± ____________.

4.2. Adequate data for accuracy in the determination are not currently available.

5. Apparatus

5.1. Sampling: Apparatus as specified in "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," shall be used.[2]

5.2. Analysis

5.2.1. Technicon II Analyzer: An automated analytical system must be used for the determination of water soluble sulfate by this method. Alkaline solutions of methylthymol blue decompose on exposure to air. The method, therefore, cannot be adapted to a manual procedure. The Technicon II Automated Analyzer System (manufactured by Technicon Instruments Corp., Tarrytown, New York 10591) consists of the following components:

5.2.1.1. Technicon Autoanalyzer Sampler IV

5.2.1.2. Proportioning Pump III: Either single speed or two speed pump for rapid flushing.

5.2.1.3. Mixing Coils: One double 11-loop mixing coil 43 mm (1.75 in.) long and 30 mm (1.25 in.) wide. One double 10-loop mixing coil 41 mm (1.63 in.) long and 30 mm (1.25 in.) wide. One 5-loop mixing coil 30 mm (1.25 in.) long and 30 mm (1.25 in.) wide.

5.2.1.4. Ion-Exchange Column: Interfering heavy metals are removed by the use of an ion-exchange resin. Use Dowex 50W-X8, sodium form, 300 to 850 μm (20-50 mesh). The resin should be stirred into distilled water and the fines discarded before they can settle. The resin should be soaked before use, at least overnight, and may be stored under distilled water until used. To pack a column, a small piece of glass wool is inserted in one end of a piece of plastic tubing 10 cm (4 in.) long and 2.3 mm (0.09 in.) I.D. A rubber pipette bulb is attached to the end of the tubing containing the glass wool plug. The other end of the tubing is placed in the soaked resin container and the rubber bulb operated until the tubing is filled with resin. The column must be free of trapped air after filling with resin. The resin column should be replaced after a full day's use.

5.2.1.5. Single Channel Colorimeter: A stable colorimeter suitable for use at 460 nm with a band width of no greater than 18 nm at half height.

5.2.1.6. Flow Cell: 15-mm path length flow cell.

5.2.1.7. Linearizer: The use of a linearizer is optional. The sulfate response does not always conform to Beer's Law. If the MTB solution (6.2.15.) is prepared with the optimum molarity and a barium chloride ratio a close approximation to Beer's Law is obtained, a linearizer is not required. However, if a linearizer is available, it may be used.

5.2.1.8. Single Channel Recorder: Strip chart recorder matched to the analyzer output.

5.2.1.9. Modular Digital Printer: Converts analog signal from the recorder to digital printout. The use of the printer is convenient but optional.

5.2.1.10. Pump Tubing: Flow rated tubing of the capacities shown in Figure 1. Deviations from these flow rates are acceptable only to the extent that a proper calibration curve and acceptable quality control checks are obtained. The use of silicone rubber tubing in place of the standard pump tubing is highly recommended for the MTB and flow cell waste lines. Pump tubing should be replaced every 21 days used.

5.2.2. Volumetric Flasks: 50, 100, 500, 1,000 ml capacity.

5.2.3. Pipettes: 2, 3, 4, 5, 6, 7, 8, 10, 15, 20, 25, 50 ml volumetric; 10 ml graduated in 1/10 ml intervals.

5.2.4. Pyrex Glass Wool

5.2.5. Plastic Tubing: 10 cm (3.94 in.) and 2.3 mm (0.09 in.) I.D.

5.2.6. Rubber Pipette Bulb

5.2.7. Buchner Funnels: Buchner style 150 ml capacity with fine-pore fritted glass filter.

5.2.8. Vaccum Filtering Apparatus: Device which permits vacuum filtering directly into the receiver. This consists of a bell jar with a top opening, a side tabulation, and a bottom plate. The Buchner funnel passes through the top opening and is sealed to the bell jar with a stopper. The bell jar should be tall enough to contain the polyethylene bottles used for storing the samples. The vacuum connection is made using the side tubulation. The filtering apparatus is shown in Figure 2.

5.2.9. Vacuum Pump: Any device which can maintain a vacuum of at least 85 KPa (64 cm of Hg). Mechanical pumps or water aspirators may be used.

5.2.10. Polyethylene Bottles: Bottles with a capacity of 60 ml (2 oz) fitted with polyseal caps.

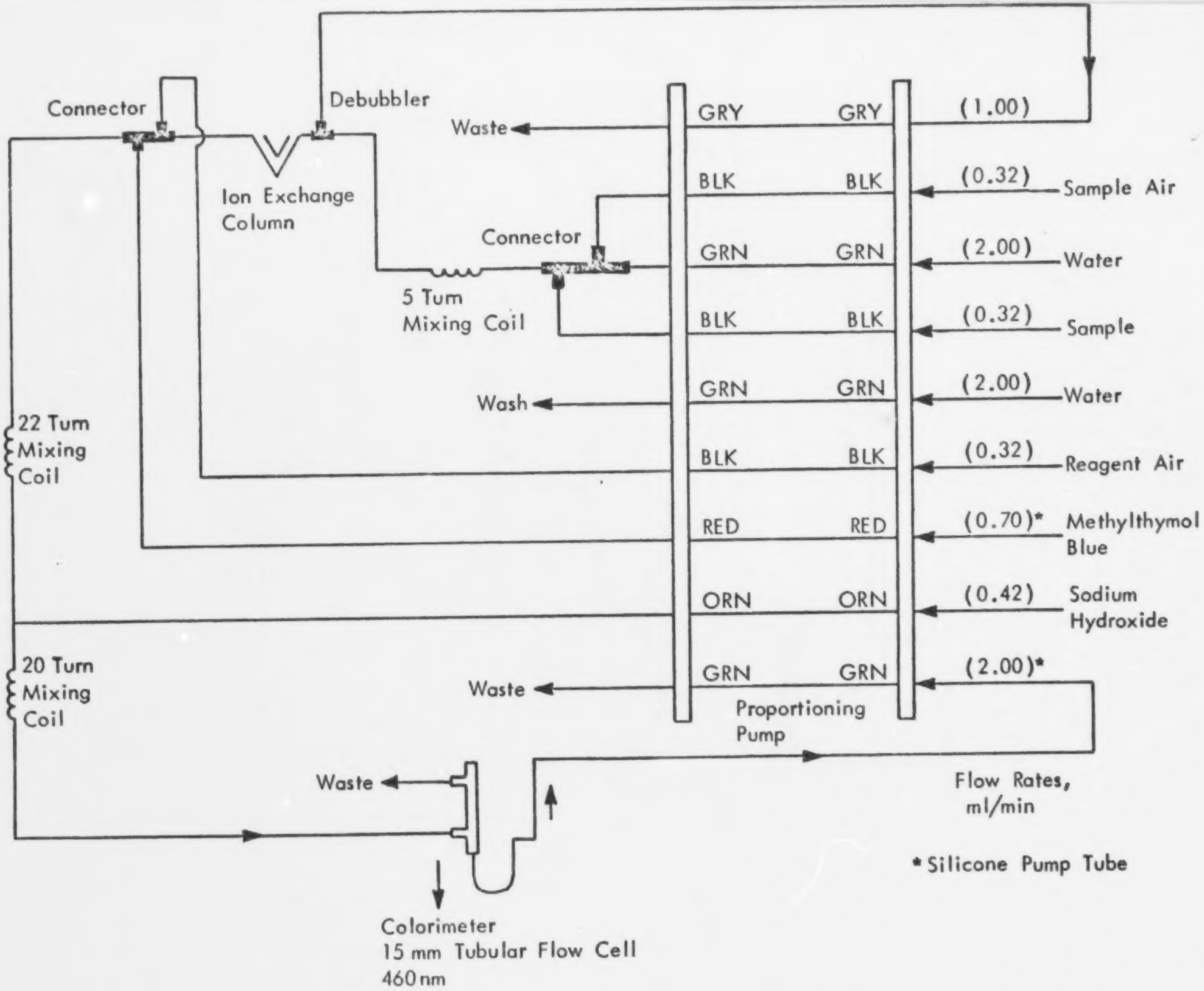
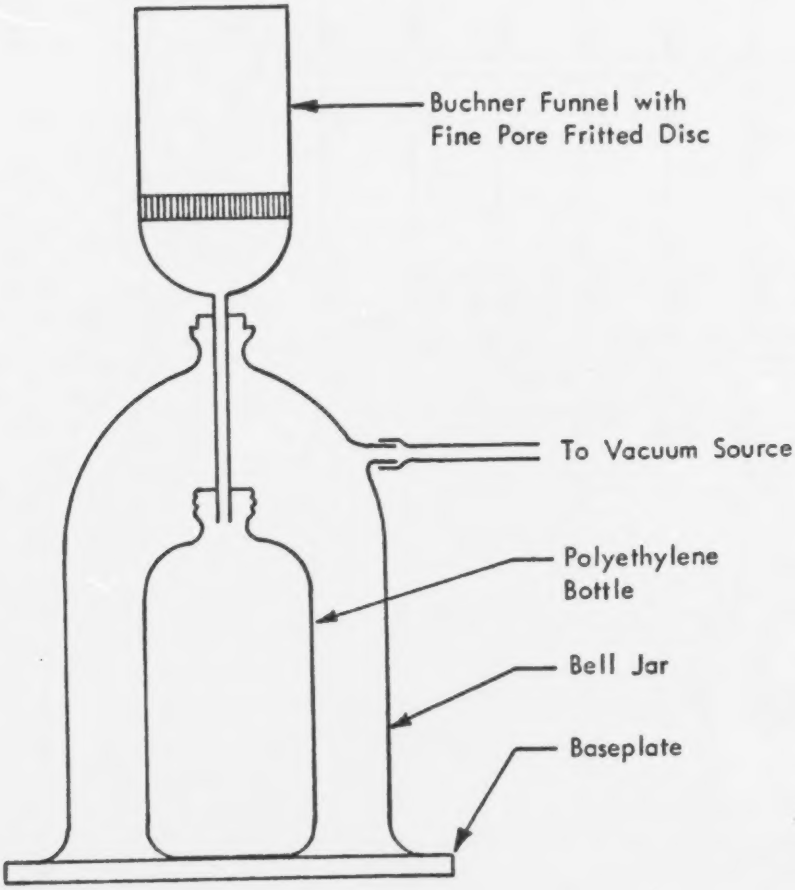

Connector
Debubbler
Waste
Ion Exchange Column
Connector
5 Turn Mixing Coil
Wash
22 Turn Mixing Coil
20 Turn Mixing Coil
Waste
Waste
GRY
GRY
BLK
BLK
GRN
GRN
BLK
BLK
GRN
GRN
BLK
BLK
RED
RED
ORN
ORN
GRN
GRN
Proportioning Pump
(1.00)
(0.32)
Sample Air
(2.00)
Water
(0.32)
Sample
(2.00)
Water
(0.32)
Reagent Air
(0.70)*
Methylthymol Blue
(0.42)
Sodium Hydroxide
(2.00)*
Flow Rates, ml/min
*Silicone Pump Tube
Colorimeter
15 mm Tubular Flow Cell
460 nm

Figure 1. Autoanalyzer Flow Diagram for Sulfate Analysis.



Buchner Funnel with Fine Pore Fritted Disc
To Vacuum Source
Polyethylene Bottle
Bell Jar
Baseplate

Figure 2. Vacuum Filtering Apparatus.

5.2.11. Glass Bottles (brown): 500-ml glass bottles with poly-seal caps.

5.2.12. Graduated Cylinder: 10 and 100-ml capacities.

5.2.13. pH Meter: Capable of measuring pH to nearest 0.1 pH unit over a range of 0 to 14.

5.3. Extraction: The samples may be extracted using either the reflux or ultrasonic procedure.

5.3.1. Ultrasonic Extractions

5.3.1.1. Ultrasonic Cleaner: Of suitable size to process the required number of samples and at least 7.6 cm (3 in.) deep.

5.3.1.2. Glass Bottles (clear): 60-ml (2-oz) glass bottles with snap polyethylene covers.

5.3.2. Reflux Extraction

5.3.2.1. Erlenmeyer Flask: 125 ml with 24/40 Ŧ joint.

5.3.2.2. Condenser: Water jacketed, 300 mm length with 24/40 Ŧ joints.

5.3.2.3. Hot Plate: Suitable for sample extraction (7.2.1.2.).

5.3.2.4. Teflon® Sleeves: Sized to fit Ŧ 24/40 joints.

6. Reagents

6.1. Sampling

6.1.1. Filter Media: Filter media as specified in "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," shall be used.[2] At least six randomly selected filters from each lot should be analyzed for sulfate, and those lots producing a blank value >1 μg/ml should be rejected.

6.1.1.1. Determination of Filter pH: Cut a 58 cm^2 (9 $in.^2$) section of glass fiber filter with a pizza cutter. Place the filter in a 125-ml Erlenmeyer flask. Add 15 ml of 0.05 M KCl (6.2.2.) and stopper the flask. Stir with a magnetic stirrer for 10 min at ≅60 rpm. Deter[illegible] the pH of the extract.

Obtain the pH for at least six randomly selected filters of a given lot of filters and report the mean and standard deviations. The pH value has an effect on accuracy of the collection procedures. Optimal pH value of the filter extract is not presently known, but pH information will be useful for historical purposes. Filters currently used in the National Air Sampling Network (NASN) have a pH of 9.74 ± 0.89.

6.1.1.2. Determination of Filter $SO_4^=$ Content: Measure the sulfate content of at least six randomly selected filters from each lot of filters. Cut a 7.6 x 20.3 cm (3/4 x 8 in.) strip from each filter using a pizza cutter and a template. Follow the procedures for extraction and analysis given in either sections 7.2.1.1. or 7.2.1.2. and 9.2.2. Calculate the mean and standard deviations in $\mu g\ SO_4^=/in.^2$. The mean standard deviations should not exceed 2.5 and 1.2 $\mu g\ SO_4^=/in.^2$, respectively. The sulfate content of filters in current use by NASN have mean and standard deviations of 2.1 and 1.1 $\mu g\ SO_4^=\ in.^2$, respectively.

6.2 Analysis

6.2.1. Sodium Hydroxide: ACS Reagent Grade.

6.2.2. Barium Chloride: ACS Reagent Grade.

6.2.3. Methylthymol Blue (MTB): 3',3"-bis[N, N-bis(carboxymethyl) amino] methyl thymolsulfone-phthalein pentasodium salt; 96% minimum by spectro analysis; Eastman No. 8068 or equivalent. The purity of commercial MTB may vary considerably. Each lot of MTB must therefore be analyzed following the procedure described in 8.1.8.

6.2.4. Ethanol: 95% U.S.P.

6.2.5. Ammonium Chloride: ACS Reagent Grade.

6.2.6. Concentrated Ammonium Hydroxide: ACS Reagent Grade, 28 to 30% as NH_3.

6.2.7. EDTA Tetra Sodium Salt: Tetra sodium ethylenediamine tetraacetate, Technical Grade.

6.2.8. Sodium Sulfate: ACS Reagent Grade, anhydrous.

6.2.9. Concentrated Hydrochloric Acid: ACS Reagent Grade, 36.5 to 38.0% HCl.

6.2.10. Distilled Water: ACS Reagent Grade, having a specific conductance of $2\ \mu\Omega^{-1}\ cm^{-1}$ or less.3/

6.2.11. Potassium Chloride: ACS Reagent Grade.

6.2.12. Sodium Hydroxide Solution (0.1 N): Dissolve 2.0 g of sodium hydroxide in distilled water and make to 500 ml in a volumetric flask.

6.2.13. Hydrochloric Acid Solution (1.0 N): Add 8.3 ml of concentrated hydrochloric acid to water in a volumetric flask and make to 100 ml.

6.2.14. Barium Chloride Solution (0.0086 M): Dissolve 2.090 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in distilled water and make to 1,000 ml in a volumetric flask.

6.2.15. Methylthymol Blue Solution (0.00038 M): To an amount equal to 0.164 g of 100% pure MTB (see section 8.2.8.) in a 500-ml volumetric flask add successively 25 ml of barium chloride solution, 4 ml of 1.0 N hydrochloric acid, and make to 500 ml with 95% ethanol. Store in a brown glass bottle. Reagent prepared one day may be used on the following day if stoppered and stored in the dark.

6.2.16. Buffer pH 10.1: Dissolve 6.75 g of ammonium chloride (NH_4Cl) in 500 ml of distilled water. Add 57 ml of concentrated ammonium hydroxide (NH_4OH) and dilute to 1,000 ml with distilled water. Adjust the pH to 10.1 with additional NH_4OH.

6.2.17. Buffered EDTA (wash solution): Dissolve 40 g of tetrasodium EDTA in the pH 10.1 buffer solution.

6.2.18. Stock Sulfate Solution (1,000 $\mu g\ SO_4^{=}/ml$): Dissolve 1.4787 g of sodium sulfate (Na_2SO_4), which has been heated at 105°C for 4 hr and cooled in a dessicator over anhydrous magnesium perchlorate, and dilute to 1,000 ml with distilled water. Store under refrigeration.

6.2.19. Blank Reagent Color Solution: To a 500-ml volumetric flask add 4 ml of 1.0 N hydrochloric acid and make to 500 ml with 95% ethanol.

6.2.20. Potassium Chloride Solution (0.05 M): Dissolve 3.7 g of KCl in 1,000 ml of CO_2 free distilled water. The pH of this solution should be 7.0 ± 0.3.

6.2.21. Wetting Agent: A 30% solution of polyoxyethylene ether of lauryl alcohol (BRIJ-35) or other suitable non-ionic wetting agent should be added at the rate of 0.5 ml/liter to the wash and sample dilution water supply.

7. Procedure

7.1 Sampling: Sampling procedures as specified in "Appendix B - Reference Method for the Determination of Suspended Particulate in the Atmosphere (High Volume Method)" shall be used.[2]

7.2 Analysis

7.2.1. Sample Extraction: The filters are removed from the folder, opened flat, and cut into 1.9 cm x 20.3 cm (3/4 in. x 8 in.) strips using a pizza cutter. The filter should be cut with the particulates face up.

7.2.1.1. Ultrasonic Extraction: One or more filter strips are placed in a 60-ml (2-oz) glass bottle. A random 5 to 10% of the filters should be extracted in duplicate for use as quality control samples.[4] Fifty milliliters of distilled water is pipetted into each bottle. The bottles are then closed with snap polyethylene caps. The samples are placed in the ultrasonic bath, which should be refilled before each set of extractions with fresh cold tap water to the level of the liquid in the bottles. The ultrasonic bath is operated for 30 min. The extracts are immediately vacuum filtered using the Buchner funnels and the vacuum filtering apparatus. The samples are filtered directly into polyethylene bottles. The filters should not be washed or squeezed, and the filtrates are not diluted. After filtering is complete, the polyethylene bottles are capped with polyseal caps and stored upright until analyzed. The samples are stable at room temperature for at least 2 weeks.

7.2.1.2. Reflux Extraction: One or more filter strips are folded and placed in a 125-ml Eerlenmeyer flask. Add 35 ml of distilled water to the flask and connect to a 300-mm water jacketed condenser. Place the flask condenser assembly on a hot plate and boil gently for 30 min. Maintain cold water circulation through the condenser while the sample cools to room temperature. Rinse the walls of the condenser with 5 ml of distilled water and disconnect the flask. Decant the liquid in the flask directly into the Buchner funnel of the filtering apparatus and filter into a glass graduated tube with a 50 ml graduation mark. Rinse the filter in the flask with a 5-ml portion of distilled water and add the rinse to the funnel. Squeeze the filter with a glass rod to remove the remaining extract and collect the filtrate. Repeat the rinse with a second 5-ml portion of distilled water. Collect the filtrate and dilute to a volume of 50 ml with distilled water. Transfer the sample to a 60-ml (2-oz) polyethylene bottle and cap with a polyseal cap. Mix thoroughly. These samples are stable at room temperature for at least 2 weeks.

7.2.2. Sample Analysis: A Technicon II Analyzer is employed for analysis. A flow diagram and reagent flow rates are shown in Figure 1, page 5. The absorbance is measured at 460 nm, and a flow cell with a path length of 15 mm is employed. The sample turntable rate is 40 samples/hr with a 12-sec wash time. The elapsed time between sample pickup and the corresponding peak is approximatley 6 min. The instrument should be zeroed and spanned following the manufacturer's directions.

The automatic analyzer is operated at the beginning of each day, after a fresh ion-exchange column is installed, and prior to the first sample analysis until a drift-free baseline is obtained. Analysis should be conducted in a laboratory with reasonable temperature control since the method is moderately affected by temperature.

7.2.2.1. Sample and Quality Control Standard Loading: Fill the test cups with samples and place on the turntable. One quality control sample, a 50 $\mu g\ SO_4^{=}$/ml calibration standard (8.2.3.), and one or two water blanks are included after every 10 samples. Establish a historical data base and construct a quality control chart indicating 3σ lower and upper control limits for the 50 $\mu g\ SO_4^{=}$/ml standard.[5] The distilled water is included after each 10th sample cup to correct for baseline drift. If the sample extracts are highly colored or contain suspended particulate, a blank must be run of the samples. This may be accomplished by replacing the MTB solution (6.2.15.) with ethyl alcohol plus acid solution (6.2.19.) and performing the analysis a second time. The sulfate values from the sample blanks should then be used in calculating the final sulfate concentration.

If a linearizer is used (5.2.1.7.), the various standards used for calibration (8.2.3.) are programmed through the linearizer so that sulfate concentrations are printed directly in micrograms per milliliter by the digital printer.

7.2.3. System Maintenance: After completing the final analysis, the system should be cleaned with the EDTA solution. With the analyzer operating, place the MTB line and NaOH line in distilled water for 2 to 3 min. Remove the ion exchange column and replace it with transmission tubing. Then transfer the MTB, NaOH lines, and the sample dilution lines to the EDTA solution container for 10 min. All liquid lines are then finally washed with distilled water for 15 min before shutting down the analyzer. The sample line may be conveniently washed during this operation by shutting off the turntable when the sample probe is in the wash position. All liquid lines should be left filled with water after the system has been washed if daily use is anticipated. If, however, the system is idle for 1 week or more, all lines must be drained and dried. During analysis a coating will slowly build up on the flow cell windows which is not completely removed by the EDTA wash. This buildup is indicated by a loss in colorimeter sensitivity and may be removed by washing the cell with 1 N HCl followed by an acetone and then a water wash.

8. Calibration

8.1. High Volume Sampler: The high volume air sampler shall be calibrated as specified in "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)."[2]

8.2. Technicon II Autoanalyzer

8.2.1. Flow Rates: The flow rates in the Autoanalyzer system should be checked when the system is originally set up. It should also be checked when any system substitutions are made. Disconnect the specific line as it leaves the pump and insert the line in a 10-ml graduated cylinder. Operate the pump for 2 min. If the flow rate is in error by more than 5%, change the pump tubing and recheck the flow.

The flow rates indicated in Figure 1 page 5 will produce the recommended reagent ratios. Minor variations in flow can be tolerated as long as they are constant, since they will be corrected for in the calibration procedure.

8.2.2. Colorimeter Wavelength: The uncomplexed MTB at a pH of 12.4 has a maximum absorbance at 460 nm. The colorimeter wavelength accuracy should be checked prior to use and annually thereafter. Maximum transmission of the filter should occur at 460 ± 15 nm.

8.2.3. Concentration Standards: Dilute 50 ml of stock sulfate solution containing 1,000 μg $SO_4^=$/ml to 500 ml with distilled water. This intermediate sulfate solution contains 100 μg $SO_4^=$/ml. If a linearizer is used, pipette 15, 35, 50, 65, 80, and 95 ml of 100 μg $SO_4^=$/ml solution into separate 100-ml volumetric flasks and dilute to the mark with distilled water. These solutions contain 15, 35, 50, 65, 80, and 95 μg $SO_4^=$/ml, respectively. If a linearizer is not used, pipette 5, 10, 10, 15, 20, 50, 60, and 75 ml of the 100 μg $SO_4^=$/ml solution into 100, 100, 50, 50, 100, 100, and 100 ml volumetric flasks and dilute to the mark with distilled water. The solutions contain 5, 10, 20, 30, 40, 50, 60, and 75 μg $SO_4^=$/ml, respectively.

8.2.4. Autoanalyzer Start Up: Start up the analyzer and start reagents flowing through the system. The sample in the flow cell must be free of bubbles during operation. Refer to manufacturer's instructions for general operating procedures. Set the sampling rate at 40, the wash time at 12 sec, the range switch at 100, and the decimal switch at 000.

Operate the instrument until a stable baseline is obtained. This normally requires a minimum of 30 min. The turntable is loaded with duplicate standards in the following sequence: 0, 100, 0, followed by low to high sulfate standards.

8.2.4.1. Operation with Linearizer: The linearizer switch is set in the direct mode and the recorder is zeroed using the baseline control and water blanks and spanned to 100% full scale using the standard calibration control and a 100 μg/ml standard. The recorder is rezeroed when the second set of water blanks reaches steady state. The linearizer is then switched to the linear mode. When the 15 μg/ml standard reaches steady state, adjust the 0 to 20 calibration control until the concentration indicator reads 15 and activate the printer. The second 15 μg/ml standard should validate the setting by indicating the correct concentration. As the 35 μg/ml standard reaches steady state, adjust the 20 to 40 calibration control until 35 μg/ml is indicated. Continue to adjust each calibration control using the standard which lies within its range until all calibration controls have been set. The calibration controls are locked in position after they have been adjusted. The adjustment of the linearizer needs to be repeated only when changing lots of MTB or when a standard varies more than 3 μg/ml from its true value.

8.2.4.2. Operation Without Linearizer: The recorder is zeroed using the baseline control and water blanks and spanned to 100% full scale using the standard calibration control and the 100 μg/ml standard. The recorder is rezeroed when the second set of water blanks reaches steady state. The remaining standards are then processed and the recorded values compared with their true values. The differences should be less than 3 μg/ml. Repeat span and zero adjustments if required. If acceptable readings cannot be obtained, check analyzer operation, flow rates, and reagent concentrations to locate problem.

When operating the automatic analyzer, air bubbles should not be allowed to enter the ion-exchange column. If air bubbles become trapped, the ion-exchange column should be replaced with a new column. A broadening of the colorimeter output with a corresponding loss in peak height usually indicates a performance decay in the pump tubing. At the first indication of peak broadening the pump tubing should be replaced. Pump tubing normally is good for at least 190 hr of operation.

8.2.5. 100% Adjustment: The full range of the recorder is used, from 0 to 100%.

8.2.6. Baseline Adjustment: The baseline is adjust to zero at the beginning and after every 10th sample using a distilled water blank.

8.2.7. Calibration Standards: Standards are run at the beginning and end of each day. If at the end of the day, the standards vary more than 3 μg/ml from their true value, the run is considered invalid and must be repeated.

8.2.8. Assay of Methylthmol Blue: The purity of commercial MTB may vary considerably. It is, therefore, necessary to determine the barium equivalency for each lot of MTB using the following procedure.

To 0.164 g of MTB in a 500-ml volumetric flask, add successively 75 ml of 0.0086 M barium chloride solution (6.2.14.), 4 ml of 1.0 N hydrochloric acid (6.2.13.), and make to 500 ml with 95% ethanol.

Pipette 2, 3, 4, 5, 6, 8, 10, 12, 14, 16, 17, 18, 19, and 20 ml of 1,000 μg $SO_4^=$/ml solution (6.12.18.) into separate 100-ml volumetric flasks and dilute to the mark with distilled water. These solutions contain 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, 170, 180, 190, and 200 μg $SO_4^=$/ml, respectively.

Start up the analyzer using the above MTB solution in place of the normal MTB solution. Operate the analyzer until a stable baseline is obtained.

Span the analyzer using the 200 μg $SO_4^=$/ml solution and proceed to analyze in triplicate all of the above sulfate solutions. The analysis should be conducted with the linearizer in the direct mode. Plot the data, micrograms $SO_4^=$/ml versus peak height, on linear graph paper. The plot will consist of three intersecting straight lines as shown in Figure 3. The intersection of the first and second portions of the plot (1) indicates the sulfate concentration required to react with the excess barium. The intersection of the second and third portions of the plot (2) indicates the sulfate concentration required to react with the complexed barium. Determine these two intersects and calculate the purity and amount of MTB to be used for reagent preparation as described in 9.1. and 9.2.

9. Calculations

$$\mu g\ SO_4^=/m^3 = \frac{[\mu g\ SO_4^=/ml_{(p)} - (\mu g\ SO_4^=/ml_{(c)} + \mu g\ SO_4^=/ml_{(b)})] \times 50 \times 12}{V}$$

where:

$\mu g\ SO_4^=/ml_{(p)}$ = printout for sample (7.2.2.1.)
$\mu g\ SO_4^=/ml_{(c)}$ = color correction (7.2.2.1.)
$\mu g\ SO_4^=/ml_{(b)}$ = blank correction. This is the $SO_4^=$ content of the filter reduced to g/ml for the mean 3/4 in. x 8 in. filter strip (6.1.1.2.).

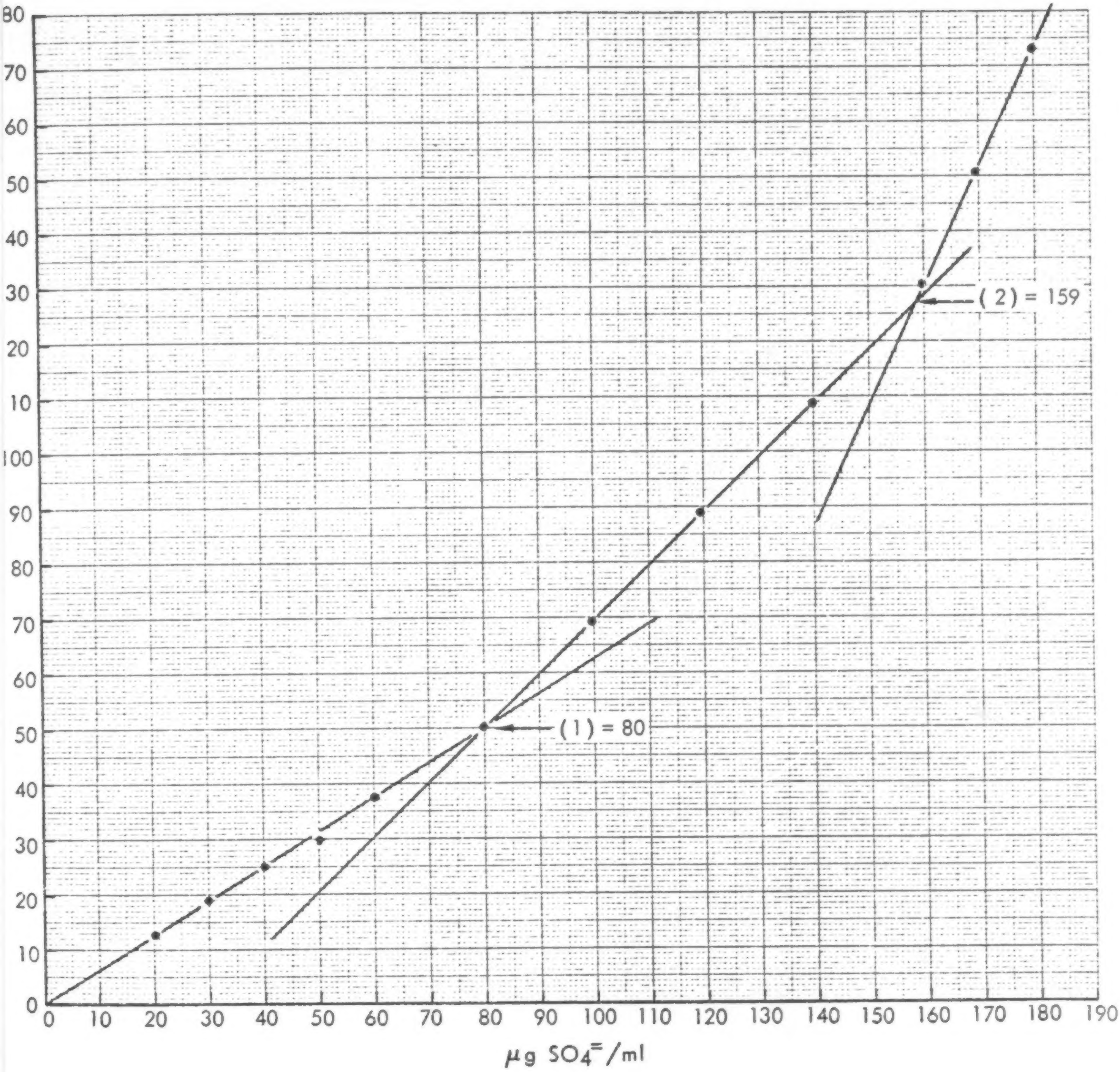


Figure 3 - Plot of MTB Assay

50 = correction to toal volume of the sample (7.21.1).
12 = correction to entire filter $SO_4^=$ content (9 ÷ 3/4) (7.2.1.).
V = total volume of air through filter, m^3 (8.1.).

9.1. Calculation of MTB Purity:

$$\% \text{ Purity} = \frac{[\mu g\ SO_4^=/ml_{(2)} - \mu g\ SO_4^=/ml_{(1)}]\ F_1 \times C \times 866.73}{W \times F_2 \times 2} \times 100$$

where:

$\mu g\ SO_4^=/ml_{(2)}$ = $\mu g/ml$ reading from second intersection point 8.2.8.
$\mu g\ SO_4^=/ml_{(1)}$ = $\mu g/ml$ reading from first intersection point 8.2.8.

F_1 = flow rate in ml/min for sample line (normally 0.32)
C = molar concentration of stock solution (normally 1.041×10^{-2})
866.74 = molecular weight of MTB
W = weight of MTB in mg
F_2 = flow rate in ml/min for MTB line (normally 0.7)
2 = value to calculate MTB concentration on basis of equivalents/liter.

9.2. Calculation of Weight of MTB:

$$\text{Weight of material for analysis} = \frac{0.164 \times 100}{\% \text{ Purity from (9.1.)}}$$

10. References

1 Lazrus, A. L., K. C. Hill, and J. P. Lodge, "A New Colorimetric Microdetermination fo Sulfate Ion." Presented at the Technicon Symposium, "Automation in Analytical Chemistry," New York, New York, September 8, 1965.

2 "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Federal Register, 36(84):8191-8194, April 30, 1971.

3 ASTM Standards (Water, Atmospheric Analysis), Part 23, October 1969 (p. 225).

4 "Guidelines for Development of a Quality Assurance Program - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," EPA Environmental Monitoring Series, EPA-R4-73-028b, June 1973.

5 ASTM Manual on Quality Control of Methods, Special Technical Publication 15-C, January 1951. Obtainable from ASTM, 1916 Race Street, Philadelphia, Pennsylvania 19103.

APPENDIX F

Protocol for Ion Chromatographic Analyses of Sulfate and Nitrate

1. Equipment

1.1 Ion-Chromatograph. Dionex System 10 Ion Chromatograph, Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94087.

1.2 Varian A-25 Recorder and Spectra-Physics Autolab Minigrator Model 23000-010. (Spectra Physics, 2905 Stender Way, Santa Clara, CA 95051)

1.3 Containers. To hold extraction solution and subsequent storage of samples, 4 oz. polypropylene containers with plastic screw-caps.

1.4 Filters (extraction). 0.45 μ disposable filter unit (Swinnex-25 Filter Unit, Millipore, or equivalent).

1.5 Syringes. 12 cc disposable syringes, without needle, graduations 0.2 cc. (Monoject Sterile Disposable Syringe, Cat. No. 512S, or equivalent)

2. Reagents

2.1 Deionized, filtered water. (D.F. H_2O for all reagents and suppressor column rinse.) To minimize introduction of background ions into the system, the water should be deionized to a resistance of approximately 15 megohms, or conductivity of 0.1 to 1.0 micromho/cm. The water should be free of particles larger than 0.20 μm to avoid the accumulation of residue or debris in the ion-exchange beads or flow system. Fill reservoir labelled "H_2O" in the chromatograph.*

---

* When filling reservoirs, avoid air bubbles which may cause pumps to lose their prime - see instruction manual for this procedure.

2.2 Eluant. Prepare 0.003 M $NaHCO_3$ - 0.0024 M Na_2CO_3 solution as follows: In a 2-liter volumetric flask, dissolve 1.008 g $NaHCO_3$ (sodium bicarbonate, MCB, Cat. No. SX320 or equivalent) and 1.0175 g Na_2CO_3 (sodium carbonate, MCB, Cat. No. SX395-CB705 or equivalent) with deionized filtered water prepared as in 2.1 above. Invert gently to dissolve, make to the mark with deionized water, mix. Transfer to the eluant reservoir labelled "E_1" or "E_2" in the chromatograph.* Add an additional 2 liters to make a total of 4 liters, and mix well.

2.3 Regenerant. Prepare 1 N H_2SO_4 as follows: Into a 2 liter volumetric flask containing approximately 1 liter of deionized filtered water, introduce 111 ml of concentrated sulfuric acid, mix, cool. Make to the mark with deionized water, mix. Fill reservoir labelled "Regenerant" in the chromatograph. Add an additional 2 liters to make a total of 4 liters, and mix well.

2.4 Stock Standard Sulfate Solution (1000 μg sulfate/ml). Dry $(NH_4)_2SO_4$ (ammonium sulfate, NBS certified) powder at 105°C for 4 hours, cool in a desiccator. Dissolve 1.376 g of the dried ammonium sulfate in deionized water and dilute to 1 liter.

2.5 Stock Standard Nitrate Solution (1000 μg nitrate/ml). Dry KNO_3 (potassium nitrate, NBS certified) powder at 105°C for 4 hours, cool in a desiccator. Dissolve 1.631 g of the dried potassium nitrate in deionized filtered water and dilute to 1 liter.

---

* When filling reservoirs, avoid air bubbles which may cause pumps to lose their prime - see instruction manual for this procedure.

2.6 Nitrate-Sulfate Working Standards. Prepare working standards of 0, 5, 10, 20, 40---160 μg/ml nitrate and sulfate concentrations. To obtain the best accuracy and precision, weigh out the required amounts of stock standards into small beakers, and then transfer the contents to Class A volumetric flasks. The samples are then bracketed by at least four standards during analysis. Samples of higher concentration (outside the 10 μmho range) are set aside, diluted, and analyzed at a later time.

Working Standard μg/ml Nitrate-Sulfate	ml or gms of Nitrate Stock Std. Added	ml or gms of Sulfate Stock Std. Added
0	0	0
5	0.50	0.50
10	1.00	1.00
20	2.00	2.00
---- 160	16.00	16.00

In each case, after addition of both stock standards to a 100 ml Class A volumetric flask, add sufficient double distilled water to the mark.

3. Analytical Procedure (Note: Read the chromatograph and integrator instruction manuals before proceeding).

3.1 Integrator-Recorder Operation. If the range of the sample is known beforehand (e.g., 0 to 80 μg/ml), it is possible to optimize the recorder response by adjusting the integrator attenuation and recorder span. For general operation on the 10 μmho to scale, so that the recorder response corresponds 1 to 1 with the Dionex meter, the controls are set as below.

Varian A-25 Recorder

Span: 1.0 volt. Adjust the recorder zero and span so that they coincide with the Dionex meter readings.

Chart Speed: 10 inches per hour, when the 3 x 500 mm anion column is used.

Minigrator Model 23000-010

The most important parameters are set as below:

Peak Width (PW) = 99

Slope Sensitivity (SS) = 99999

Baseline (BL) = 1.0

Trailing Peak (TP) = 1

The following parameters are inactivated: MA, SP, PL, B_1, B_2, and T_2. T_1 is set at a time which eliminates early peaks, just prior to elution of the nitrate curve. (Determine by experience)

3.2 Put the toggle switch on the front panel of the chromatograph in the LOAD position; using a syringe, inject 2 ml of sample solution into the injection port. Leave the syringe in place during chromatography.

3.3 Using the OFFSET COARSE or FINE knobs, adjust the indicator needle on the SPECIFIC CONDUCTANCE meter to 0.0.

3.4 Flip the toggle switch to the INJECT position, at the same time start the integrator or strip chart. After 15-30 seconds, flip the toggle switch back into the LOAD position.

3.5 Record the sample I.D. on the chart.

3.6 After the run is completed, rinse the sample loop with 3 ml of deionized filtered water with the toggle switch still in the LOAD position.

3.7 Inject the next sample as described in Sections 3.2 through 3.6.

Note: The system will use approximately 4 liters of eluant per day.

4. Chromatograph Start-Up (Review Ion-Chromatograph Instrument Manual)

4.1 Using the regulator on a dry air or nitrogen compressed gas cylinder, adjust the pressure to 90-100 psi for the air actuated valves in the chromatograph. Flip the toggle labelled AIR, on the front panel of the chromatograph, to the ON position.

4.2 Flip the toggle labelled POWER to the ON position.

4.3 Place the toggle labelled FLUSH down.

4.4 Place the toggle labelled $\frac{\text{INJECT}}{\text{LOAD}}$ down.

4.5 Place the toggle labelled $\frac{E_1}{\text{WATER}}$ up.

4.6 Place the toggle labelled E_2 up if E_1 is empty.

4.7 Place the toggle labelled E_2 down if reservoir E_1 is full.

4.8 Place the toggle labelled ANALYT up.

4.9 Place the toggle labelled SUPPRESS up.

4.10 Flip the toggle labelled PUMP to the ON position. Adjust the vernier dial on the front pump so that the flow rate is appropriate, e.g., 2.5 ml min. (The flow rate may be checked by disconnecting the output tubing from the suppressor column and placing the tubing in a graduated cylinder). Allow the system to run for 30 minutes before beginning the integrator calibration, or until the baseline drift is reasonably stable. Check for leaks in the tubing connections. Wear safety glasses when opening the column door. Check reservoir levels.

4.11 Turn MODE switch to LIN.

4.12 Turn μMHO FULL SCALE to 10.

4.13 Set SPECIFIC CONDUCTANCE needle to 5.0 or 10.00 with the OFFSET COARSE and FINE knobs. (Allow sufficient positive baseline to account for any negative drift).

5. Standards and Calibration

5.1 Inject 3 ml of each of the standards described in paragraph 2.6. Record the reading by automatic integration and by measuring the recorder trace (chromatogram) peak height.

5.2 Calculate regression lines separately for nitrate and sulfate plotting recorder response versus concentration.

6. Regeneration of Suppressor Column

6.1 At the end of each day's run, the suppressor column required regeneration as indicated by a color change in the column resin bed from tan to whitish tan, or by a swift rise in the conductance.

6.2 On the chromatograph, make the following settings:

6.2.1 Flip toggle switch labelled PUMPS to the OFF position. Set the switch labelled MODE to ZERO.

6.2.2 Flip toggle switch labelled SUPPRESS to the down position. Check the liquid levels in the regenerant and "H_2O" reservoirs.

6.2.3 Set TIME MIN indicators to 10 on REG side and 50 on RIN side.

6.2.4 Depress the green button labelled START, the rear pump should begin pumping. Set the vernier on the rear pump to approximately 90.

6.2.5 The cycle of regeneration is now automatic. At the end of the cycle, the pump will stop and the suppressor column will be tan colored. The cycle may be stopped prematurely by depressing the red colored button labelled RESET.

7. Chromatograph Shut Down

7.1 Flip the toggle switch labelled PUMP to the OFF position.

7.2 If the regeneration cycle is in process, and premature termination is necessary, depress the red button labelled RESET.

7.3 Make sure the integrator is off (LINE button has been depressed and indicator lights are off).

7.4 Flip toggle switch labelled POWER to the OFF position.

7.5 Flip AIR toggle switch to the OFF position.

7.6 Turn off regulator on compressed air or nitrogen cylinder.

7.7 Protect the integrator from dust using a plastic cover.

7.8 If the chromatograph is to be shut down for a long period of time (e.g., 2 months) rinse both columns with distilled water beforehand.

APPENDIX G

Protocol for Extraction of Organics from Aqueous Extracts of Atmospheric Particulates for Use in Interference Studies of Sulfate Methods

Objective

To extract the organics from aqueous extracts from atmospheric particulate matter without co-extraction of sulfate.

Procedure

About 2400 ml of an aqueous extract obtained from extraction at 85-100°C of 60 loaded 8 x 10" hi-vol filter samples was filtered through Whatman #2 filter paper. The filtrate was transferred into three 2 liter beakers and evaporated on a steam bath to about 0.6 liter (total). This was acidified with HCl and the 0.6 liter extracted with three 100 ml portions of 1:1 v/v butanol-chloroform. The aqueous phase was evaporated to near dryness and extracted with 100 ml of butanol-chloroform. The 400 ml of organic extract was washed twice with 100 ml distilled water. No sulfate could be detected in the wash water (tested with aminoperimidine). The organic solvent was then evaporated to dryness on the steam bath. The brown, resinous residue was dissolved in 20 ml water containing 0.5 ml of 4 N NH_4OH in a petri dish. The petri dish was heated for 5 minutes to evaporate excess ammonia. The solution was diluted and filtered with washing into a 250 ml volumetric flask and made up to 250 ml with distilled water.

Result

The pH of the solution so obtained was 6.5 and the color intensity about 2 at λ = 400 nm. Comparison of this absorbance with that of the remaining yellow aqueous solution indicated 64% extraction of the chromophoric organics. The colored organics in the remaining solution was hydrophilic at all pH values and could not be easily extracted or freed of sulfate.

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Environmental Research Information Center
Cincinnati, Ohio 45268

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE. $300
AN EQUAL OPPORTUNITY EMPLOYER

POSTAGE AND FEES PAID
U S ENVIRONMENTAL PROTECTION AGENCY
EPA-335

U.S.MAIL

If your address is incorrect, please change on the above label tear off; and return to the above address.
If you do not desire to continue receiving these technical reports, CHECK HERE ☐; tear off label, and return it to the above address,

EPA-600/4-79-028

B359/9